# ANALYTICA CHIMICA ACTA

Vol. 25 (1961)

732

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*International monthly dealing with every branch of analytical chemistry*
*Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique*
*Internationale Monatsschrift für alle Gebiete der analytischen Chemie*

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*Anal. Chim. Acta*, Vol. 25 (1961)

Printed in the Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

# ANALYTICA CHIMICA ACTA VOL. 25 (1961)

# AUTHOR INDEX

Adams, R. N., see Larson, R. C.
——, see Mueller, T. R.
Alfonsi, B. . . . . . 274, 374
Altshuller, A. P., I. R. Cohen, M. E. Meyer and A. F. Wartburg Jr. . . 101
Ariel, M. and J. Manka . . . . . . 248
Ashraf, M., M. K. Bhatty and R. A. Shah 448
Balt, S., see Van Dalen, E.
Barendrecht, E. . . . . . 402
Belcher, R. and J. E. Fildes . . . . . 34
Berg, E. W. and H. L. Youmans . 366, 470
Berka, A. . . . . . 434
Berka, A., J. Doležal, J. Janata and J. Zýka . . . . . 379
——, J. Doležal, I. Němec and J. Zýka 533
Berman, S. S., see Russell, D. S.
Bhat, A. N. and B. D. Jain . . . . . 343
Bhatnagar, M. L., see Majumdar, R.
Bhatty, M. K., see Ashraf, M.
Bloch, L. . . . . . 404
Bouissières, G., see Merinis, J.
Burriel-Martí, F., see Pino Pérez, F.
Cameron, A. J. and N. A. Gibson . 24, 429
Campbell, J. B., see Russell, D. S.
Capelle, R. . . . . . 59
Cohen, E.M., see Lordi, N.G.
Cohen, I. R., see Altshuller, A. P.
Connors, K. A. and T. Higuchi . . . . 509
Cornet, C., see Ducret, L.
Cover, R. E. and L. Meites . . . . . 93
Daftary, R. D. and B. C. Haldar . . . 538
Davis, D. K., see Knight, J. A.
De, A. K., see Majumdar, S. K.
Dey, A. K., see Singh, E. J.
Diffee, J., see West, Ph. W.
Doležal, J., see Berka, A.
Drushel, H. V., see Senn Jr., W. L.
Ducret, L. and C. Cornet . . . . . 542
Duewell, H., see Hawkins, C. J.
Duval, G. R., R. Ironside and D. S. Russell . . . . . 51
Fildes, J. E., see Belcher, R.
Florence, T. M. and D. B. Izard . . . 386
Garnett, J. L., W. K. Hannan and S. W. Law . . . . . 170
Gaur, J. N., N. K. Mathur and D. C. Sanchetti . . . . . 176
——, see Panwar, K. S.
——, see Rao, S. P.
Gianni, F. and F. Potenza . . . . . 90
Gibson, N. A., see Cameron, A. J.
Gillespie, A., see Weiss, H. V.
Glasö, Ö. and G. Patzauer . . . . . 189
Golterman, H. L. and I. M. Wurtz . . 295
Govett, G. J. S. . . . . . 69
Gowda, H. S. and W. I. Stephen . . . 153
Grant, D. and D. S. Payne . . . . . 422
Greenhalgh, R. and J. P. Riley . . . 179
Hadjioannou, T. P. and C. Vassiliades 516
Haldar, B. C., see Daftary, R. D.
Hannan, W. K., see Garnett, J. L.
Hara, R., see Nomura, S.
——, see Umezawa, H.
Havre, G. N. . . . . . 557
Hawkins, C. J., H. Duewell and W. F. Pickering . . . . . 257
Hazel, J. F., see Katz, S. A.
Hennart, C. . . . . . 150, 201
Higuchi, T., see Connors, K. A.
Huré, J., M. Rastoix and R. Saint-James . . . . . 1, 118
Ingalls, R. B. and G. A. Pearson . . . 566
Ironside, R., see Duval, G. R.
Iwamoto, R. T., see Larson, R. C.
Izard, D. B., see Florence, T. M.
Jacobsen, E. and A. R. Selmer-Olsen 476
Jain, B. D., see Bhat, A. N.
Janata, J., see Berka, A.
Janauer, G. E., see Korkisch, J.
Jungreis, E. and A. Lerner . . . . . 199
Katz, S. A., W. M. McNabb and J. F. Hazel 193
Khorasani, S. S. M. A. and M. H. Khundkar . . . . . 292
Khundkar, M. H., see Khorasani, S. S. M. A.
Kienberger, C. A., see Petit, G. S.
Knight, J. A., B. Wilkins Jr., Davis, D. K. and F. Sicilio . . . . . 317
Korkisch, J. and G. E. Janauer . . . 463
——, see Tera, F.
Krall, A. R. and L. P. Zill . . . . . 457
Kristiansen, H. . . . . . 513
Langmyhr, F. J. and O. B. Skaar . . . 262
Larson, R. C., R. T. Iwamoto and R. N. Adams . . . . . 371
Law, S. W., see Garnett, J. L.
Lerner, A., see Jungreis, E.
Lindley, G. . . . . . 334
Locke, D. and J. Sherma . . . . . 312
Lordi, N. G. and E. M. Cohen . . . . 281
Lorica, A. S., see West, Ph. W.
McNabb, W. M., see Katz, S. A.
Majumdar, R. and M. L. Bhatnagar . . 203
Majumdar, S. K. and A. K. De . . . . 452
Malát, M. . . . . . 289
Malissa, H. and L. J. Ottendorfer . . 461
Manka, J., see Ariel, M.
Mapper, D., see Smales, A. A.
Maros, L., E. Schulek, I. Molnár-Perl and M. Pintér-Szakács . . . . . 390
——, M. Pintér-Szakács and E. Schulek 546
Mateo, F. J., see Pino Pérez, F.
Mathur, N. K., see Gaur, J. N.
Meditsch, J. O., see Ohlweiler, O. A.
Meites, L., see Cover, R. E.
Merinis, J. and G. Bouissières . . . . 498
Meyer, M. E., see Altshuller, A. P.
Ming Gon Lai, see Weiss, H. V.
Molnár-Perl, I., see Maros, L.

Mosen, A. W., R. A. Schmitt and J. Vasilevskis 10
Mottola, H. A. and E. B. Sandell 520
Mueller, T. R. and R. N. Adams 482
Murty, G. V. L. N. and T. S. Viswanathan 293
Němec, I., see Berka, A.
Noe, J. L., see Sawicki, E.
Nomura, S. and R. Hara 212
Ohlweiler, O. A. and J. O. Meditsch 233
Ottendorfer, L. J., see Malissa, H.
Panalaks, T. 598
Panwar, K. S., S. P. Rao and J. N. Gaur 218
Pâris, R. A., see Thomas, G.
Patzauer, G., see Glasö, Ö
Payne, D. S., see Grant, D.
Pearson, G. A., see Ingalls, R. B.
Petit, G. S. and C. A. Kienberger 579
Pickering, W. F., see Hawkins, C. J.
Pino Pérez, F., F. Burriel-Martí and F. J. Mateo 207
Pintér-Szakács, M., see Maros, L.
Potenza, F., see Gianni, F.
Rakshpal, R., see Taimni, I. K.
Rao, S. P., see Panwar, K. S.
——, H. S. Rathi and J. N. Gaur 136
Rastoix, M., see Huré, J.
Rathi, H. S., see Rao, S. P.
Riley, J. P., see Greenhalgh, R.
Ruggieri, R. 145
Russell, D. S., J. B. Campbell and S. S. Berman 81
——, see Duval, G. R.
Saint-James, R., see Huré, J.
Sanchetti, D. C., see Gaur, J. N.
Sandell, E. B., see Mottola, H. A.
Sawicki, E. and J. L. Noe 166
Schmitt, R. A., see Mosen, A. W.
Schulek, E., see Maros, L.
Selmer-Olsen, A. R., see Jacobsen, E.
Senn Jr., W. L. and H. V. Drushel 328
Serpinet, J. 505
Seyfang, A. P., see Smales, A. A.
Shah, R. A., see Ashraf, M.
Sharp, J. 139
Sherma, J., see Locke, D.
Shibata, S. 348
Sicilio, F., see Knight, J. A.
Singh, E. J. and A. K. Dey 57
Skaar, O. B., see Langmyhr, F. J.
Smales, A. A., D. Mapper and A. P. Seyfang 587
Stephen, W. I., see Gowda, H. S.
Stiller, M. 85
Taimni, I. K. and R. Rakshpal 438
Tera, F. and J. Korkisch 222
Testa, C. 525
Thomas, G. and R. A. Pâris 159
Tufts, B. J. 322
Umezawa, H. and R. Hara 360
Van Dalen, E. and S. Balt 507
Van Erkelens, P. C. 42, 129, 226, 570
Van Wesemael, J. Ch. 238
Vasilevskis, J., see Mosen, A. W.
Vassiliades, C., see Hadjioannou, T. P.
Viswanathan, T. S., see Murty, G. V. L. N.
Wartburg Jr., A. F., see Altshuller, A. P.
Weber, J. N. 270
Weiss, H. V., Ming Gon Lai and A. Gillespie 550
West, Ph. W. and A. S. Lorica 28
——, and J. Diffee 399
West, T. S. 301, 405
Wilkins Jr., B., see Knight, J. A.
Wurtz, I. M., see Golterman, H. L.
Youmans, H. L., see Berg, E. W.
Zill, L. P., see Krall, A. R.
Zýka, J., see Berka, A.

## ANALYTICA CHIMICA ACTA VOL. 25 (1961)

## SUBJECT INDEX

Acetonitrile, voltammetry in ——, reference electrodes, (Larson, Iwamoto, Adams) 371
$\beta$-Alanine, solvent extraction of oxidation products, (Panalaks) 598
Alcohols, aliphatic, oxidation by $KMnO_4$, (Sharp) 139
——, spectrophotometry of small amounts, (Stiller) 85
Aldehydes, aliphatic, analysis of —— in source effluents and in the atmosphere, (Altshuller, Cohen, Meyer, Wartburg) 101
——, aromatic ——, polarometry with 2,4-dinitrophenylhydrazine, (Berka, Doležal, Janata, Zýka) 379
Aldoximes, pyridine and 1-methylpyridinium ——, polarography, (Lordi, Cohen) 281
Alizarin–lanthanum complexone in the determination of fluoride in natural water, (Greenhalgh, Riley) 179
Aluminium, cathode ray polarography of —— in Be metal, (Florence, Izard) 386
——, determination in zinc-base die-casting alloys, (Bloch) 404
——, EDTA titration with 3-hydroxy-2-naphthoic acid as indicator, (Kristiansen) 513
——, specific test, (Jungreis, Lerner) 199
Amines, thermometry, (Daftary, Haldar) 538

α-Amino acids, oxidimetry with vanadium(V), (Rao, Rathi, Gaur) . . 136

4-Aminoazobenzene-1-naphthylamine, reagent for nitrites and $NO_2$, (Sawicki, Noe) . . . . . . . . . . 166

Ammonium purpurate, spectrophotometry of Sr with ——, (Russell, Campbell, Berman) . . . . . . . . 81

Antimony(III), separation by ion exchange, (Khorasani, Khundkar) . . . 292

Arsenic–iron alloys, analysis, (Duval, Ironside, Russell) . . . . . . . 51

Azo compounds, determination of N, (Ashraf, Bhatty, Shah) . . . . 448

Azomethine-H, in the colorimetry of B in steels, (Capelle) . . . . . . . . 59

5-Benzaminoanthraquinone-2-sulphonic acid as reagent for detection and gravimetry of Na, (Gowda, Stephen) . . . . . . . . . . . . . . 155

Beryllium metal, cathode ray polarography of Al in ——, (Florence, Izard) . 386

——, determination of U in —— by neutron activation and γ-spectroscopy, (Smales, Mapper, Seyfang) 587

Bismuth, determination of traces with dithizone after iodide extraction, (Mottola, Sandell) . . . . . . 520

Boric acid in pharmaceutical glass, analysis with 1,8-dihydroxyanthraquinone, (Ruggieri) . . . . . . . . . . . 145

Boron carbide electrodes, oxidation of ferrocyanide and o-dianisidine, (Mueller, Adams) . . . . . . . . 482

Boron, determination in steels, (Capelle) 59

——, spectrography of —— in nuclear graphite, (Gianni, Potenza) . . . 90

——, spectrophotometry with 1,1′-dianthrimide, (Langmyhr, Skaar) . 262

Bromine, Cl, I, simultaneous determination in organic compounds, (Belcher, Fildes) . . . . . . . . 34

Cadmium, spot test with glyoxal-bis(2-hydroxyanil), (West, Diffee) . . . 399

Calcium, cation-exchange behaviour on Dowex 50W-X8, (Majumdar, De) 452

——, flame-photometry in plant extracts, (Hávre) . . . . . . . . . . . . 557

Carbamate-forming metals, detection in presence of Al by ring oven and spot colorimetry, (Malissa, Ottendorfer) . . . . . . . . . . . . . . . 461

Carbon, determination in Si and Ge, (Ducret, Cornet) . . . . . . . . . 542

Carbon dioxide, distillation at atmospheric pressure, titrimetry, (Maros, Schulek, Molnár-Perl, Pintér-Szakács) . . . . . . . . . . . . . 390

—— distillation, analytical application, (Maros, Pintér-Szakács, Schulek) . . . . . . . . . . . . 546

Cation analysis, qualitative, by differential precipitation ionography, (Tufts) 322

Cerium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10

Cerium(IV) sulphate solutions in sulphuric acid, effect of heat, (Grant, Payne) 422

Chelatometry, aspects of increasing selectivity, (West) . . . . . . . . 301

——, see also EDTA titrations

Chlorine, Br, I, simultaneous determination in organic compounds, (Belcher, Fildes) . . . . . . . . 34

Chromatography, flow monitor for scanning $^{32}P$-effluents, (Krall, Zill) . . . 457

Chromazurol S, dissociation constants, (Malát) . . . . . . . . . . . . 289

Chromium, and V, separation and photometry, (Katz, McNabb, Hazel) 193

——, EDTA titration with extractive endpoint, (Cameron, Gibson) . . . . 429

——, spectrophotometry with o-dianisidine, (Ariel, Manka) . . . . . . 248

Chromium(II), in the potentiometry of Tl(III), (Majumdar, Bhatnagar) 203

Citrate as complexing agent in the chromatography of ions, (Singh, Dey) . . 57

Cobalt, determination of traces, (Van Erkelens) . . . . . . . 42, 129, 226

——, EDTA titration with extractive endpoint, (Cameron, Gibson) . . . . 24

——, spectrophotometry with 1,2-diaminocyclohexanetetraacetic acid, (Jacobsen, Selmer-Olsen) . . . 476

Copper, determination of traces, (Van Erkelens) . . . . . . . 42, 129, 226

——, EDTA titration with extractive endpoint, (Cameron, Gibson) . . . . 429

Coulometry, pilot-ion, with dropping Hg electrodes, (Cover, Meites) . . . 93

Cyanide, determination of traces, (Murty, Viswanathan) . . . . . . . . 293

1,2-Diaminocyclohexanetetraacetic acid in spectrophotometry of Co, (Jacobsen, Selmer-Olsen) . . . . . . 476

o-Dianisidine, oxidation at $B_4C$ electrodes, (Mueller, Adams) . . . . . . . 482

——, in the spectrophotometry of Cr and V, (Ariel, Manka) . . . . . . . 248

1,1′-Dianthrimide, in the spectrophotometry of boron, (Langmyhr, Skaar) . . . . . . . . . . . . 262

1,8-Dihydroxyanthraquinone, as reagent for boric acid in pharmaceutical glass, (Ruggieri) . . . . . . . 145

*vic*-Diketones, EDTA titration, (Hennart) 201

2,4-Dinitrophenylhydrazine, in polarometry of aromatic aldehydes, (Berka, Doležal, Janata, Zýka) . . . . . 379

2,4-Dinitrophenylhydrazones, solvent extraction system for ——, (Panalaks) . . . . . . . . . . . . 598

*vic*-Dioximes, EDTA titration, (Hennart) 150

Diphenylcarbazide, reactions with cations (Van Dalen, Balt) . . . . . . . 507

Diphenylcarbazone, reactions with cations, (Van Dalen, Balt) . . . . 507

Distribution procedures, gas-, liquid-, solid-phase, separation of traces of inorganic ions, (West) . . . . . . 405
Dithizone, in determination of traces Bi after iodide extraction, (Mottola, Sandell) . . . . . . . . . . . 520
Dysprosium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . 10
EDTA titration, of Al, and stepwise EDTA titration of Al and Fe(III), (Kristiansen) . . . . . . . . . . . 513
——, of Co with extractive end-point, (Cameron, Gibson) . . . . . . . 24
——, of *vic*-diketones, (Hennart) . . . . 201
——, of *vic*-dioximes, (Hennart) . . . . 150
——, with extractive end-points, (Cameron, Gibson) . . . . . . . . . . 429
——, see also chelatometry
Electrolysis, controlled-potential ——, of Pb alloys, (Alfonsi) . . . . . . . 274
——, ——, of Sn alloys, (Alfonsi) . . . 374
Erbium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Ethanol, oxidation by $KMnO_4$, (Sharp) . 139
Europium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Ferrocyanide, oxidation at $B_4C$ electrodes, (Mueller, Adams) . . . . . . . 482
Fluoride, determination in natural waters, (Greenhalgh, Riley) . . . . . 179
Formic acid, determination by oxidation with HgCl, (Maros, Pintér-Szakács, Schulek) . . . . . . . . . 546
Gadolinium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Gases, permanent ——, gas chromatography with a helium detector, (Serpinet) . . . . . . . . . . . . 505
Germanium, determination of C in ——, (Ducret, Cornet) . . . . . . . 542
Glyoxal bis-(2-hydroxyanil), spot test for Al, (Jungreis, Lerner) . . . . . 199
——, spot test for Cd, (West, Diffee). . 399
Gold target, separation by volatilization of radioisotopes of Pt, Ir, Os, Rh formed by bombardment of ——, (Merinis, Bouissières) . . . . . 498
Graphite, nuclear, spectrography of B in ——, (Gianni, Potenza). . . . . 90
Hafnium, separation of Zr from ——, data of chemical equilibria, (Huré, Rastoix, Saint-James) . . . . . . 1, 118
Halogens, microdetermination in organic compounds, (Belcher, Fildes). . 34
Heat effect on $Ce(SO_4)_2$ solutions in $H_2SO_4$, (Grant, Payne) . . . . . . . . 422
Helium detector, gas chromatography of permanent gases with ——, (Serpinet) . . . . . . . . . . . . 505
Holmium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Hydrazine as reagent in iodimetry, (Panwar, Rao, Gaur) . . . . . . . . 218
3-Hydroxy-2-naphthoic acid as indicator in EDTA titration of Al and Fe(III), (Kristiansen) . . . . . . 513
*p*-(3-Hydroxy-3-phenyltriazeno)-phenyltrimethylammonium chloride, colour reagent for metal ions, (Gaur, Mathur, Sancheti) . . . . . . . 176
Iodate, potassium ——, in potentiometry of uric acid, (Berka) . . . . . . 434
Iodide, solvent extraction method for separation of ——, (West, Lorica) . 28
Iodimetry, hydrazine as reagent in ——, (Panwar, Rao, Gaur) . . . . . . 218
Iodine, Cl, Br, simultaneous determination in organic compounds, (Belcher, Fildes) . . . . . . . . . . . 34
Ionography, differential precipitation ——, for qualitative cation analysis, (Tufts) . . . . . . . . . . 322
Iridium, radioisotopes, separation by volatilization, (Merinis, Bouissières) 498
——, spectrophotometry with $SnI_2$, (Berg, Youmans) . . . . . . . . . . . 470
Iron–arsenic alloys, analysis, (Duval, Ironside, Russell) . . . . . . . 51
Iron, determination of traces, (Van Erkelens) . . . . . . . . . 42, 129, 226
——, EDTA titration with extractive end-point, (Cameron, Gibson) . . . . 429
——, in blood, automatic titration, (Hadjioannou, Vassiliades) . . . . 516
——, ore, determination of silica in ——, (Glasö, Patzauer) . . . . . . . 189
Iron(II), spectrophotometry, with oximidobenzotetronic acid, (Bhat, Jain) . 343
——, ——, with substituted 1,10-phenanthroline compounds, (Hawkins, Duewell, Pickering). . . . . . . 257
Iron(III), EDTA titration with 3-hydroxy-2-napthoic acid as indicator, (Kristiansen) . . . . . . . . . 513
——, liquid-liquid extraction with 2-thenoyltrifluoroacetone, (Testa) . . . 525
Keidel electrolytic hygrometer, modified, determination of traces of water in gases, (Barendrecht) . . . . . . 402
Lanthanum–alizarin complexone in the determination of fluoride in natural waters, (Greenhalgh, Riley) . . 179
Lanthanum in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis). . 10
Lead-base alloys, controlled-potential electrolysis, (Alfonsi) . . . . . . . 274
Lead, determination of traces, (Van Erkelens) . . . . . . . . . 42, 129, 226
——, paper chromatography with phosphate-$^{32}P$, (Van Erkelens) . . . 570
Lead(IV) acetate in oxidimetry of Tl(I), (Berka, Doležal, Němec, Zýka) 533

Lutetium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10

Magnesium determination, in zinc-base die-casting alloys, (Bloch) . . . . 404

——, with titan yellow, (Van Wesemael) 238

Manganese, determination of traces, (Van Erkelens) . . . . . . . . 42, 129, 226

Mercury(II) chloride in the determination of formic acid, (Maros, Pintér-Szakács, Schulek) . . . . . . . 546

Methanol, oxidation by $KMnO_4$, (Sharp) 139

Methyl isobutyl ketone in the separation of Cr and V, (Katz, McNabb, Hazel) . . . . . . . . . . . . . . 189

1-Methylpyridinium aldoximes, polarography, (Lordi, Cohen) . . . . . . 281

Molecular weight determination, semi-micro cryoscopic ——, (Knight, Wilkins, Davis, Sicilio) . . . . . . 317

Molybdenum, determination of traces, (Van Erkelens) . . . . 42, 129, 226

Monochloroselenodiphenylamine as reagent for Pd, (Pino Pérez, Burriel-Martí, Mateo) . . . . . . . . . 207

Murexide, spectrophotometry of Sr with ——, (Russell, Campbell, Berman) . . . . . . . . . . . . . 81

Neodymium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis). . 10

Neutron-activation analysis, determination of rare earths in meteorites, (Mosen, Schmitt, Vasilevskis). . 10

Nickel, EDTA titration with extractive end-point, (Cameron, Gibson) . . 429

Nicotine, thermometry, (Daftary, Haldar) . . . . . . . . . . . . 538

Nitrites, determination with 4-aminoazobenzene-1-naphthylamine, (Sawicki, Noe) . . . . . . . . . . . . 166

Nitro compounds, determination of N, (Ashraf, Bhatty, Shah) . . . . 448

Nitrogen, determination in nitro, nitroso, azo compounds, elimination of distillation in the Kjeldahl method, (Ashraf, Bhatty, Shah) . . . . 448

Nitrogen dioxide, determination with 4-aminoazobenzene-1-naphthylamine, (Sawicki, Noe) . . . . . . . . . 166

Nitroso compounds, determination of N, (Ashraf, Bhatty, Shah) . . . . 448

α-Nitroso-β-naphthol in the determination of U in sea water, (Weiss, Ming Gon Lai, Gillespie) . . . . . . . . . 550

Organic composition analysis, by gas chromatography and IR spectrophotometry, (Senn, Drushel) . . . . . 328

Osmium radioisotopes, separation by volatilization, (Merinis, Bouissières) 498

Oxalate as complexing agent in the chromatography of ions, (Singh, Dey) 57

Oximidobenzotetronic acid, spectrophotometry of Fe(II), (Bhat, Jain) . . 343

Oxygen, dissolved, ESR spectroscopy, (Ingalls, Pearson) . . . . . . . 566

Palladium, monochloroselenodiphenylamine as reagent for ——, (Pino Pérez, Burriel-Martí, Mateo) . . . . . 207

Pantothenate, Calcium ——, solvent extraction of hydrolyzed ——, (Panalaks) . . . . . . . . . . . . . 598

Periodate, potassium ——, in potentiometry of uric acid, (Berka) . . . . . 434

1,10-Phenanthroline compounds, substituted, (Hawkins, Duewell, Pickering) . . . . . . . . . . . 257

Phenols, paper solubilization chromatography, (Locke, Sherma) . . . . . . 312

Phosphate, inorganic, determination in presence of labile phosphate esters, (Golterman, Wurtz) . . . . . . 295

Phosphate-$^{32}$P, paper chromatography of Pb, (Van Erkelens) . . . . . . 570

Phosphorus, absorptiometry in irons and steels, (Lindley) . . . . . . . . 334

——, flow monitor for scanning effluents containing $^{32}$P from chromatography columns, (Krall, Zill) . . . 457

——, organo —— compounds, in the extraction of U, (Nomura, Hara) . . 212

Phosphorusorgano compounds in the extraction of Zr, (Umezawa, Hara) 360

Photometric indicator titration data, graphical analysis, (Connors, Higuchi) . . . . . . . . . . . . . 509

Platinum radioisotopes, separation by volatization, (Merinis, Bouissiéres) 498

Potassium, flame-photometry in plant extracts, (Havre) . . . . . . . . 557

——, permanganate, in the oxidation of aliphatic alcohols, quantitative aspects, (Sharp) . . . . . . . . . 139

——, spectrochemistry in geological materials, (Weber) . . . . . . . . . 270

Praseodymium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis). . 10

Pyridine, aldoximes, polarography, (Lordi, Cohen) . . . . . . . . . . . 281

——, thermometry, (Daftary, Haldar) 538

1-(2-Pyridylazo)-2-naphthol, solvent extraction and spectrophotometry of metals, (Shibata) . . . . . . . . . 348

Quinaldates, metallic, thermogravimetry in determining the hydration of ——, (Thomas, Pâris) . . . . . . 159

Radioisotopes of Pt, Ir, Os, Rh by volatilization, (Merinis, Bouissières) . . 498

Rare earths in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis). . 10

Rhenium radioisotopes, separation by volatilization, (Merinis, Bouissières) 498

Rhodium, spectrophotometry with $SnI_2$, (Berg, Youmans) . . . . . . . . 366

Ring oven method, detection of carbamate-forming metals in presence of Al by

—— and spot colorimetry, (Malissa, Ottendorfer) . . . . . . . 461
Samarium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Selenium, organo —— compounds, as reagent for Pd, (Pino Pérez, Burriel-Martí, Mateo) . . . . . . 207
——, salts in inorganic analysis, (Taimni, Rakshpal) . . . . . . . . . . . 438
Silica, colorimetry, (Govett) . . . . . . 69
——, determination in iron ore, (Glasö, Patzauer) . . . . . . . . . . . . 189
Silicium, determination of C in ——, (Ducret, Cornet) . . . . . . . . . . 542
Sodium, detection and gravimetry with 5-benzaminoanthraquinone-2-sulphonic acid, (Gowda, Stephen) . . 155
——, flame-photometry in plant extracts, (Havre) . . . . . . . . . . . . . . 557
Solochromate fast red, spectrophotometry of U, (Korkisch, Janauer) . . . 463
Solubilization chromatography, paper ——, of phenols, (Locke, Sherma) . . . 312
Solvent extraction, and spectrophotometry of metry of metals with 1-(2-pyridylazo)-2-naphthol, (Shibata) . . . . 348
——, method for separation of iodide, (West, Lorica) . . . . . . . . 28
Spectroscopy, ESR, determination of dissolved $O_2$, (Ingalls, Pearson) . . 566
Stannous iodide, spectrophotometry of Ir, (Berg, Youmans) . . . . . . . . 470
——, spectrophotometry of Rh, (Berg, Youmans) . . . . . . . . . . . . 366
Strontium, spectrophotometry with murexide, (Russell, Campbell, Berman) . . . . . . . . . . . . . . 81
Sulphate, absorptiometry in waters, (Ohlweiler, Meditsch) . . . . . . . . 233
Tamarium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Tartrate as complexing agent in the chromatography of ions, (Singh, Dev) 57
Terbium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilveskis) . . . 10
Thallium(I), oxidimetry with Pb(IV) acetate, (berka, Doležal, Němec, Zýka) . . . . . . . . . . . . . 533
Thallium(III), potentiometry with Cr(II), (Majumdar, Bhatnagar) . . . . . . 203
2-Thenoyltrifluoroacetone in liquid–liquid extraction of Fe(III), (Testa) . . 525
Thermogravimetry, in determining the hydration of metallic quinaldates, (Thomas, Pâris) . . . . . . . 159
Thermometry of amines, pyridine, nicotine, (Daftary, Haldar) . . . . . 538
Tin-base alloys, controlled-potential electrolysis, (Alfonsi) . . . . . . . 374
Titan yellow, in the determination of Mg, (Van Wesemael) . . . . . . . . 238
Titration data, graphical analysis of photometric indicator ——, (Connors, Higuchi) . . . . . . . . . . . 509
Traces of inorganic ions, separation by gas-, liquid-, solid-phase distribution procedures, (West) . . . . . . 405
Tritium gas counting procedure, (Garnett, Hannan, Law) . . . . . . . . . 170
Uranium, determination, in Be metal by neutron activation and $\gamma$-spectrometry, (Smales, Mapper, Seyfang) 587
——, ——, in seawater, by co-crystallisation with $\alpha$-nitroso-$\beta$-naphthol, (Weiss, Ming Gon Lai, Gillespie) 550
——, extraction with organo-P compounds, (Nomura, Hara) . . . . 212
——, preparation of stoichiometric $U_3O_8$, (Petit, Kienberger) . . . . . . 579
——, separation by ion exchange, (Tera, Korkisch) . . . . . . . . . . . 222
——, spectrophotometry with solochromate fast red, (Korkisch, Janauer) . . . . . . . . . . . . 463
Uric acid, potentiometry with $KIO_3$ or $KIO_4$, (Berka) . . . . . . . . . 434
Vanadium, and Cr, separation and photometry, (Katz, McNabb, Hazel) . 189
——, EDTA titration with extractive end-point, (Cameron, Gibson) . . . . 429
——, spectrophotometry with *o*-dianisidine, (Ariel, Manka) . . . . . . . 248
Vanadium(V), in the oxidimetry of $\alpha$-amino acids, (Rao, Rathi, Gaur) . . 136
Voltammetry, at inert electrodes, (Mueller, Adams) . . . . . . . . . . 482
——, reference electrodes for —— in acetonitrile, (Larson, Iwamoto, Adams) . . . . . . . . . . . . . 371
Water, determination of traces in gases with modified Keidel electrolytic hygrometer, (Barendrecht) . . . 402
Ytterbium in meteorites, determination by neutron-activation analysis, (Mosen, Schmitt, Vasilevskis) . . . 10
Zinc-base die-casting alloys, determination of Mg and Al in ——, (Bloch) . . 404
Zinc, determination of traces, (Van Erkelens) . . . . . . . . 42, 129, 226
Zirconium, extraction with organo-P compounds, (Umezawa, Hara) . . 360
——, separation from Hf, data of chemical equilibria, (Huré, Rastoix, Saint-James) . . . . . . . . . . . 1, 118

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

## Vol. 25, No. 1, July 1961

### RELATIVE DATA OF CHEMICAL EQUILIBRIA GOVERNING THE SEPARATION OF ZIRCONIUM FROM HAFNIUM

#### I. DETERMINATION OF EQUILIBRIUM CURVES

*(in French)*

Factors influencing the extraction of macro amounts of zirconium by tributylphosphate and his separation of zirconium from hafnium are discussed.

J. Huré, M. Rastoix and R. Saint-James *Anal. Chim. Acta*, 25 (1961) 1–9

### A PROCEDURE FOR THE DETERMINATION OF THE RARE EARTH ELEMENTS, LANTHANUM THROUGH LUTETIUM, IN CHONDRITIC, ACHONDRITIC AND IRON METEORITES BY NEUTRON-ACTIVATION ANALYSIS

The abundances of the rare earths, lanthanum through lutetium, have been determined in chondritic, achondritic, and iron meteorites by neutron-activation analysis. The procedure used should also be applicable to the analysis of terrestrial stones and sediments. After exposure to a thermal-neutron flux of $2 \cdot 10^{12}$ neutrons/cm$^2$/sec for 2 h, the chondritic or achondritic sample, with added rare earth carriers, is dissolved after sodium peroxide fusion. Iron specimens are dissolved in a hydrochloric acid medium. The rare earths are then separated as a group from the matrix and are individually separated by means of a Dowex 50 W-X12 cation resin column and elution with 1 *M* ammonium lactate. This method is sensitive to fractional parts per million of the individual rare earths. The abundance of scandium may also be determined in the same procedure.

A. W. Mosen, R. A. Schmitt and J. Vasilevskis, *Anal. Chim. Acta*, 25 (1961) 10–24

### EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

#### I. DETERMINATION OF COBALT

A method for the determination of cobalt by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending upon the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the estimation of cobalt in highly coloured aqueous solutions. Average errors can be expected to be less than 0.5%.

A. J. Cameron and N. A. Gibson, *Anal. Chim. Acta*, 25 (1961) 24–27

## A SOLVENT EXTRACTION METHOD FOR THE SEPARATION OF IODIDE

Solvent extraction is proposed for the isolation of anions. Data obtained in the extraction of iodide using cadmium as complexing agent under the influence of such factors as pH, addition of excess cadmium ions, initial concentration of the cadmium iodide solution and temperature are presented.

P. W. West and A. S. Lorica, *Anal. Chim. Acta*, 25 (1961) 28–33

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## TITRIMETRIC METHODS FOR THE MICRO DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

### II. THE SIMULTANEOUS DETERMINATION OF THE HALOGENS IN THE PRESENCE OF EACH OTHER

The absorption of the gaseous combustion products from the rapid, empty tube combustion procedure has been studied. Organic compounds containing any combination of chlorine, bromine, and iodine as well as oxygen, nitrogen and sulphur have been examined. Several methods based on established titration procedures have been developed for the simultaneous microdetermination of any two or all three halogens in organic materials.

R. Belcher and J. E. Fildes, *Anal. Chim. Acta*, 25 (1961) 34–41

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## ON THE CONCENTRATION AND SEPARATION OF THE TRACE ELEMENTS: Fe, Cu, Zn, Mn, Pb, Mo and Co

### I. ION EXCHANGE METHODS

Cation-exchange materials and selective elution with acetone–hydrochloric acid mixtures are used to concentrate the constituents of biological ashes and to separate them into the groups: $MoO_4^{-2}$, $SO_4^{-2}$, $PO_4^{-3}$; $Fe^{+3}$, $Zn^{+2}$, $Pb^{+2}$, $Cu^{+2}$; $Co^{+2}$, $Mn^{+2}$; $Na^{+}$, $K^{+}$, $Ca^{+2}$ and $Mg^{+2}$.

P. C. van Erkelens, *Anal. Chim. Acta*, 25 (1961) 42–50

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## ANALYSIS OF ARSENIC–IRON ALLOYS

Contrary to expectation and to published recommendation it is not possible to separate Fe(III) quantitatively from As(V) on a cation-exchange resin. Ion-exchange can however be utilised for the analytical separation of iron and arsenic if the iron is reduced to Fe(II) before the mixture is passed through the cation-exchange column.

G. R. Duval, R. Ironside and D. S. Russell, *Anal. Chim. Acta*, 25 (1961) 51–56

## CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, USING AQUEOUS ETHANOL AS SOLVENT. II

The separation of Al, Cr(III), Fe(III), Zn, Mn(II), Ni, Co, Ba, Sr, Ca, Mg, Na, K and $NH_4$ in ternary mixtures with or without the addition of complexing agents (oxalate, tartrate and citrate) by filter paper strip chromatography has been studied with aqueous ethanol as solvent.

E. J. SINGH AND A. K. DEY, *Anal. Chim. Acta*, 25 (1961) 57–58

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## COLORIMETRIC MICRODETERMINATION OF BORON IN STEELS WITH AZOMETHINE-H AS REAGENT

*(in French)*

A method is described for the determination of soluble and insoluble boron in steels based on preliminary separation with ion-exchange resin and colorimetric determination by means of azomethine-H.

R. CAPELLE, *Anal. Chim. Acta*, 25 (1961) 59–68

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## CRITICAL FACTORS IN THE COLORIMETRIC DETERMINATION OF SILICA

The development of rapid colorimetric analytical techniques for silicates has catalysed many fundamental research programs in the geological sciences. Despite a multitude of papers on the silicomolybdate colorimetric technique for the analysis of silica which appear in the journals of nearly all sciences, it was found extremely difficult to adapt any published method for a particular purpose, and obtain reliable results. This is due to a lack of appreciation of the factors which control the silicomolybdate reaction. Data are given which indicate that the major factors are the polymer species of molybdate, which is controlled largely by the pH of molybdate stock solution; the concentration of molybdate; the ratio of acid to molybdate in reaction; and the type of acid used in the reaction. The effect of these variables is outlined, and an analytical procedure for both "soluble" and total silica outlined.

G. J. S. GOVETT, *Anal. Chim. Acta*, 25 (1961) 69–80

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## THE SPECTROPHOTOMETRIC DETERMINATION OF STRONTIUM WITH MUREXIDE (AMMONIUM PURPURATE)

A procedure for the spectrophotometric estimation of $\mu$g-quantities of strontium with murexide is described. Conditions for the optimum stability of the coloured strontium complex have been determined, the main feature being the addition of large quantities of ethylene glycol to the system. Most elements interfere so that it is necessary to isolate the metal before the determination.

D. S. RUSSELL, J. B. CAMPBELL AND S. S. BERMAN, *Anal. Chim. Acta*, 25 (1961) 81–84

## SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS

A spectrophotometric method for the determination of small amounts of methyl, ethyl, butyl and amyl alcohols is described. The sensitivity of the method is of the order of 10 $\mu$g/ml of test solution in the case of butyl and amyl alcohols and 20–30 $\mu$g/ml in the case of ethyl and methyl alcohols. The molar extinction coefficient rises with the molecular weight of the alcohol. The nature of the alcoholic complex is not yet known.

M. Stiller, *Anal. Chim. Acta*, 25 (1961) 85–89

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## SPECTROGRAPHIC DETERMINATION OF BORON IN NUCLEAR GRAPHITE

A spectrographic method is described for the determination of boron (0.2–1.0 p.p.m.) in nuclear graphite and for the estimation of 0.1–0.2 p.p.m. of boron. Neither boron-free graphite electrodes nor additional foreign substances as internal standard are required. Both the electrodes consist of sample powder, properly bakelite-processed. The standard deviation is 10%.

F. Gianni and F. Potenza, *Anal. Chim. Acta*, 25 (1960) 90–92

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## PILOT-ION COULOMETRY WITH DROPPING MERCURY ELECTRODES

The theory and the experimental and chemical requirements of pilot-ion coulometry with the dropping mercury electrode are outlined, and several examples are given of its application to the determination of *n*-values for half-reactions occurring in polarographic experiments.

R. E. Cover and L. Meites, *Anal. Chim. Acta*, 25 (1961) 93–96

# DONNÉES RELATIVES AUX ÉQUILIBRES CHIMIQUES RÉGISSANT LA SÉPARATION ZIRCONIUM–HAFNIUM

## I. ÉTABLISSEMENT DES COURBES D'ÉQUILIBRE

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(Reçu le 21 novembre 1960)

### INTRODUCTION

Lorsque fut publié pour la première fois à Genève le procédé de séparation du zirconium et de l'hafnium par le phosphate tributylique[1], les teneurs préconisées pour la solution de zirconium alimentant l'extracteur étaient les suivantes: Zr: 10 g/l; $HNO_3$: 3 *N*; $NaNO_3$: 3.5 *M*.

Nos conditions de travail actuelles sont les suivantes, pour cette même solution: Zr: 60 g/l; $HNO_3$: 6 *N*; $NaNO_3$: néant.

Ce sont tout d'abord les études nous ayant conduits à ces modifications que nous présenterons ici. Nous examinerons ensuite le problème de la "3ème phase", phase bien connue de tous ceux qui ont utilisé le phosphate tributylique (TBP) en mélange avec un solvant paraffinique, pour l'extraction du zirconium et du thorium et qui consiste en une démixtion du solvant en 2 phases, l'une riche en TBP, l'autre en diluant paraffinique.

Enfin, nous aborderons le problème du "vieillissement" du solvant et de sa régénération.

(*1*) *Suppression du nitrate de sodium.* Bien que plus favorable que l'acide nitrique à une bonne séparation du zirconium de l'hafnium, l'usage de $NaNO_3$ en exploitation industrielle comporte certains inconvénients: plus cher et moins pur que l'acide nitrique, il augmente la viscosité de la solution et, par conséquent, le temps de décantation. De plus, sa présence interdit la récupération de l'acide nitrique, facteur important du prix de revient. Il a donc été décidé d'établir les courbes d'équilibre complètes pour le zirconium et pour l'hafnium, pris isolément, à différentes concentrations et différentes acidités en présence d'acide nitrique seul.

(*2*) *Interaction Zr–Hf.* La séparation est meilleure que les coefficients de partage respectifs du zirconium et du hafnium ne le laissent prévoir, indiquant une interaction sur laquelle, à notre connaissance, aucun chiffre n'a été publié. Nous traiterons principalement de l'influence du rapport Zr/Hf sur l'extraction de Hf.

(*3*) Au delà d'une certaine teneur en zirconium et en acide nitrique, on constate, lors de l'extraction en ampoule à décanter, l'apparition d'une deuxième phase solvant. Les anglais **Hudswell** *et al.*[2] ont publié les résultats d'essais systématiques sur ce sujet. Malheureusement, ils ne relient pas cette apparition à la concentration en zirconium des phases solvant, mais uniquement à la concentration de la phase aqueuse de départ. Or, en production industrielle, où les rapports de débits, les acidités et les températures des solutions risquent de varier, il importe de connaître la concentration limite du zirconium dans le solvant, avant l'apparition de la 3ème phase. Les résultats intéressants du rapport anglais demandent à être complétés.

(*4*) Enfin, la dernière partie de notre exposé traitera de l'évolution du solvant, en milieu acide, en présence ou en l'absence de zirconium et en fonction du temps; cette étude devant être complétée par des essais synthétiques permettant d'apprécier l'influence des produits connus de l'hydrolyse du solvant, sera faite à la température ambiante.

## MODE OPÉRATOIRE

### *Méthodes analytiques utilisées*

*Dosages volumétriques*

La concentration en zirconium ou hafnium de la phase aqueuse est déterminée par voie complexométrique en utilisant le fer ferrique comme titrant et l'acide salicylique comme indicateur[3].

Le zirconium dans le solvant est dosé de la même manière, après précipitation à la potasse alcoolique et redissolution en milieu aqueux; ce mode de dosage étant utilisé pour des teneurs supérieures à 5 mg Zr dans la prise d'essai.

*Dosages colorimétriques*

Pour les faibles teneurs en zirconium, on utilise la colorimétrie du composé zirconium–acide chloranilique en milieu perchlorique, telle qu'elle est pratiquée depuis longtemps au laboratoire[4].

*Dosages acidimétriques*

Il est important de connaître "l'acidité libre" de la phase aqueuse. Ce dosage sera fait par potentiométrie de la neutralisation par la soude; on déduira du résultat trouvé, l'acidité due au zirconium qu'on suppose être, pour simplifier, sous la forme $ZrO^{+2}$, c'est-à-dire consommant 2 molécules d'hydroxyde de sodium par molécule, pour sa neutralisation. Cette hypothèse donne à tout le moins un point de repère, valable dans des conditions opératoires toujours identiques.

*Utilisation des traceurs radioactifs*

Pour étudier l'interaction Zr–Hf dans le processus d'extraction, nous avons choisi d'utiliser $^{181}$Hf comme traceur, ce qui permettait d'éviter les méthodes longues comme la spectrographie. On dosera donc Hf par comptage et Hf + Zr par volumétrie.

### *Préparation des solutions*

*Solution nitrique de zirconium*

Nous disposons d'une tourie (30 l) d'une solution contenant 107 g/l de zirconium, 2.6 g/l d'hafnium et 6.66 moles d'acide nitrique libre. Cette solution mère sera ajustée aux conditions de concentration et d'acidité voulues.

*N.B.* On constate que la solution mère n'est pas stable, se trouble et dépose très lentement. Sa concentration a varié en six mois de 107 à 100 g/l. Toutefois, après filtration, cette solution donne des coefficients de partage indépendants de son âge.

*Solutions de traceurs*

La solution contenant le traceur Hf est préparée par attaque, à l'acide nitrique fumant, de son oxyde irradié (l'attaque est d'ailleurs longue et souvent incomplète). Les solutions filtrées sont ensuite ajustées selon les besoins. On vérifie par comptage et volumétrie que le comportement de ces solutions est bien identique à celui de la solution inactive.

*Préparation du solvant*

Le tributylphosphate est dilué, comme il est courant, avec du white spirit dans la proportion: TBP 60%, white spirit 40%, en volume. Le white spirit est un solvant paraffinique désaromatisé de densité 0.75 et de point d'ébullition compris entre 130° et 190°. Préalablement à l'extraction, le solvant est acidifié de manière à réduire au maximum l'échange d'acide nitrique pour que le zirconium puisse être raisonnablement considéré comme intervenant seul dans le transfert.

Ceci n'est qu'une première approximation, dont le degré de précision dépend et de l'acidité et de la concentration en zirconium, mais l'approximation est inchiffrable puisqu'on ignore quels ions de Zr existent en solution et qu'on ne sait pas définir rigoureusement l'acidité libre d'une solution de zirconium.

Quoiqu'il en soit, pour les extractions 4, 5, 6 ou 8 *N*, on acidifiera donc le solvant en l'agitant pendant quelques minutes avec un volume égal d'une solution d'acide nitrique 4, 5, 6 ou 8 *N*. Le solvant ainsi acidifié peut être conservé pendant quatre ou cinq jours. Nous avons vérifié par ailleurs que, en ce qui concerne l'extraction, des lots de TBP de différentes origines se comportaient de manière comparable.

*Extraction*

Des volumes égaux de phase aqueuse et de phase solvant, en général 10 ml, sont mis en présence dans une ampoule à décanter et agités à la main pendant deux minutes environ. Les volumes respectifs des phases ne varient pratiquement pas ($<3\%$). On prélève ensuite une aliquote de phase aqueuse et de phase solvant, dans lesquelles on fait le dosage. Dans le cas où l'on a apparition d'une troisième phase, on note le volume respectif de chaque phase et sa concentration en zirconium.

## RÉSULTATS

### *Extraction du zirconium par le TBP*

Nous avons cherché à tracer les courbes de partage du zirconium à diverses concentrations et dans différents milieux nitriques. Les dosages ont été faits par volumétrie, systématiquement dans les phases aqueuses, pour vérification seulement dans les phases solvants.

Un milieu nitrique 4 *N* doit s'entendre: milieu contenant 4 moles d'acide nitrique libre. Les résultats sont reproduits sur le Tableau I (*cf.* Fig. 1).

Le Tableau I nous donne déjà quelques éléments sur l'importance de la teneur en zirconium de la phase solvant au moment où elle se sépare en deux. Plus la solution est acide, mieux le zirconium s'extrait, ce qui explique la constatation faite par

TABLEAU I

PARTAGE DE Zr ENTRE UNE PHASE AQUEUSE NITRIQUE ET LE SOLVANT ACIDE

| *Acidité N* | *g/l $\varphi_a$ départ* | *Vol. $\varphi_a$ à l'éq.* | *Vol. $\varphi_s$ à l'éq.* | *g/l $\varphi_a$ à l'éq.* | *g/l $\varphi_s$ à l'éq.* | *Vol. 3ème $\varphi$* | *g/l $\varphi$ 3* | *E%* | *$\alpha_{Zr}$* |
|---|---|---|---|---|---|---|---|---|---|
| 4 | 1.03 | 10 | 10 | 0.47 | 0.56 | | | 54.8 | 1.19 |
| 4 | 5.16 | 10 | 10 | 3.04 | 2.12 | | | 41.2 | 0.69 |
| 4 | 10.3 | 10 | 10 | 7.2 | 3.1 | | | 34 | 0.49 |
| 4 | 20.6 | 10 | 10 | 16 | 4.6 | | | 22.4 | 0.28 |
| 4 | 23.2 | 10 | 10 | 18.2 | 5 | | | 21.6 | 0.27 |
| 4 | 25.8 | 10 | 10 | 20.5 | 5.3 | | | 20.5 | 0.25 |
| 4 | 41.2 | 10 | 10 | 34 | 7.2 | | | 17.5 | 0.21 |
| 4 | 61.8 | 10 | 10 | 52 | 9.8 | | | 15.9 | 0.18 |
| 5 | 0.9 | 10 | 10 | 0.2 | 0.7 | | | 77.8 | 3.5 |
| 5 | 5.82 | 10 | 10 | 1.82 | 4 | | | 68.8 | 2.2 |
| 5 | 9.25 | 10 | 10 | 3.93 | 5.32 | | | 57.5 | 1.36 |
| 5 | 17.2 | 10 | 10 | 8.8 | 8.4 | | | 48.8 | 0.95 |
| 5 | 28.8 | 10 | 10 | 16.8 | 12 | | | 41.6 | 0.71 |
| 5 | 52.8 | 10 | 10 | 33.2 | 19.6 | | | 37.2 | 0.59 |
| 5 | 68.8 | 10 | 9.6 | 46.6 | 22.2 | 0.4 | indosable | 32.3 | |
| 6 | 1.03 | 10 | 9.6 | 0.13 | 0.90 | | | 87.5 | 6.65 |
| 6 | 5.60 | 10 | 9.6 | 0.88 | 4.72 | | | 84.2 | 5.36 |
| 6 | 10.2 | 10 | 9.6 | 1.84 | 8.40 | | | 82.4 | 4.56 |
| 6 | 13.8 | 10 | 9.6 | 3.24 | 10.6 | | | 76.7 | 3.27 |
| 6 | 13.9 | 10 | 9.6 | 3.41 | 10.5 | | | 75.5 | 3.08 |
| 6 | 17.1 | 10 | 9.6 | 4.30 | 12.8 | | | 75.0 | 2.98 |
| 6 | 19.7 | 10 | 9.6 | 5.38 | 14.3 | | | 72.5 | 2.66 |
| 6 | 27.3 | 10 | 9.6 | 9.50 | 17.8 | | | 65.2 | 1.87 |
| 6 | 30.9 | 10 | 9.6 | 11.2 | 19.7 | | | 63.7 | 1.76 |
| 6 | 35.0 | 10 | 9.6 | 13.7 | 21.3 | | | 60.8 | 1.55 |
| 6 | 36.7 | 10 | 9.6 | 14.7 | 22.0 | | | 60.0 | 1.50 |
| 6 | 37.1 | 10 | 9.6 | 15.1 | 22.0 | | | 59.4 | 1.45 |
| 6 | 48.0 | 10 | 8.5 | 21.5 | 26.5 | 1.5 | non dosé | 55.2 | 1.23 |
| 6 | 59.8 | 9.5 | 8.5 | 28.3 | 31.5 | 2 | non dosé | | |
| 6 | 69 | 9.5 | 8.5 | 35.3 | 33.7 | 2 | non dosé | | |
| 6 | 77 | 9.5 | 8.4 | 40 | 39.7 | 2.1 | non dosé | | |
| 6 | 96.4 | 9.5 | 8 | 53.3 | 43.1 | 2.5 | non dosé | | |
| 8 | 20.6 | 10 | 10 | 0.92 | 19.7 | | | 95.6 | 21.9 |
| 8 | 41.2 | 10 | 7.8 | 7.5 | 42.5 | 2.4 | 0.32 | 79.1 | |
| 8 | 61.8 | 10 | 7.8 | 13.9 | 61.2 | 2.5 | 0.79 | 75.7 | |

HUDSWELL suivant laquelle la troisième phase apparaît pour une concentration en zirconium, d'autant plus faible dans la phase aqueuse, que l'acidité de cette même phase est plus élevée. La concentration limite en zirconium dans le solvant au moment de l'apparition de la 3ème phase, se situerait à 22–25 g/l. Nous reviendrons plus loin sur ce problème.

La Fig. 2 donne une autre représentation du phénomène d'extraction. $\alpha_{Zr}$ n'est autre que la pente de la courbe précédente.

Par suite de l'intérêt présenté par le milieu d'acidité "libre" 6 *N* (intérêt dont nous trouverons la justification dans la suite de ce texte), nous avons été amenés à étudier ce milieu avec particulièrement de soin. Par la méthode des moindres carrés, nous avons ensuite déterminé la courbe théorique représentant le mieux les résultats expérimentaux. On trouvera sur la Fig. 3 le tracé de la courbe théorique (qui est une hyperbole) par rapport aux points expérimentaux, lesquels donnent une bonne idée de la reproductibilité des résultats.

### *Extraction du hafnium par le TBP*

Les dosages ont été faits par complexométrie pour les concentrations supérieures à 5 mg Hf/ml, et par colorimétrie au-dessous. Les modes opératoires sont bien entendu les mêmes que pour le zirconium, seul l'étalonnage change. Les résultats sont reproduits sur le Tableau II et les Figs. 3 et 4.

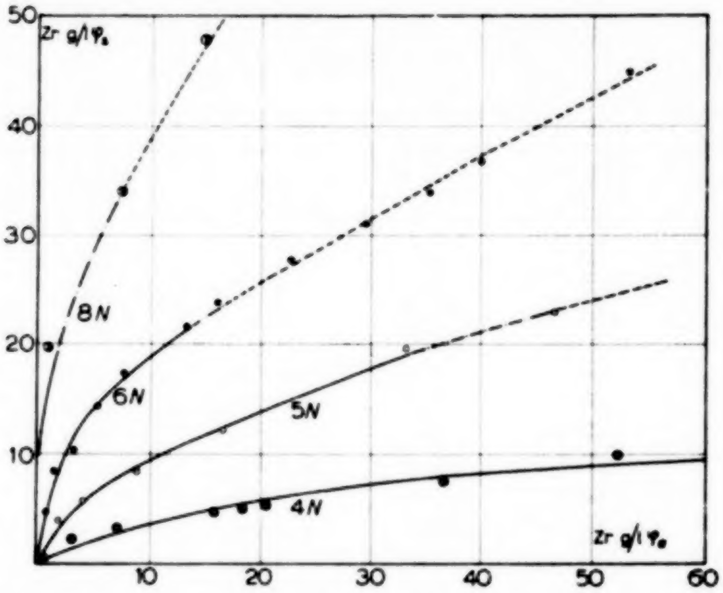

Fig. 1. Distribution de Zr à diverses concentrations en $HNO_3$. ——— 2 phases, - - - - 3 phases, - · - · - zone d'apparition de la 3ème phase.

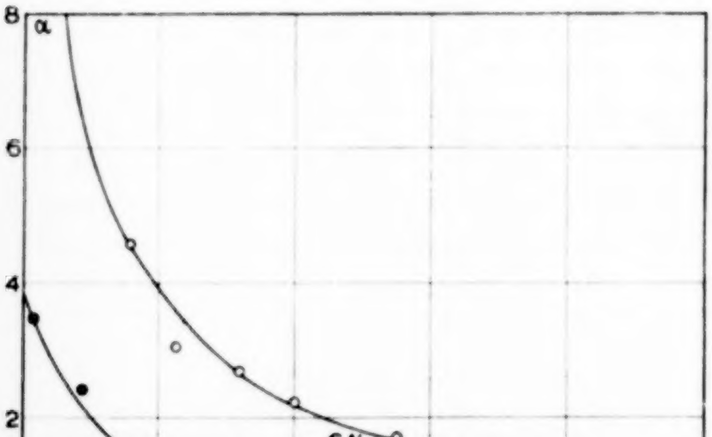

Fig. 2. Coefficient de partage $\alpha_{Zr}$.

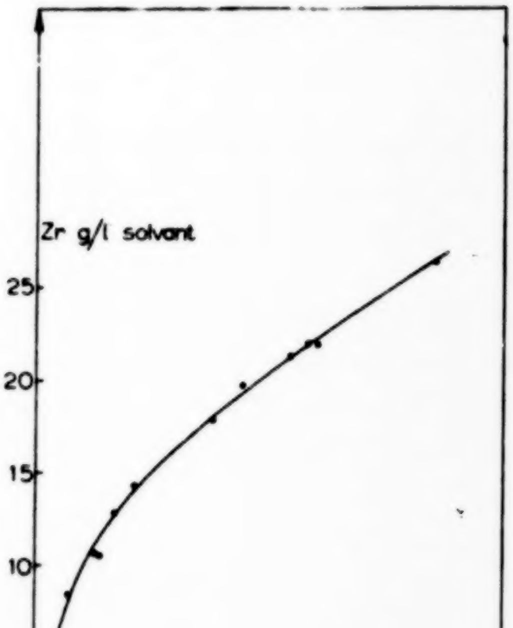

Fig. 3. Extraction Zr en milieu nitrique 6 *N*. ——— courbe théorique; . . . . points expérimentaux.

Si nous examinons maintenant les trois Tableaux et les courbes représentant nos résultats, quelques remarques s'imposent:

(*1*) La précision sur la détermination de $\alpha_{Hf}$ est très mauvaise pour les faibles teneurs ($< 1$ g/l). Ceci est dû au fait que nous nous trouvons dans une partie de courbe très verticale où de très faibles variations ont une influence notable, et également à l'imprécision des dosages à ces teneurs.

(*2*) $\alpha_{Hf}$ reste très inférieur à 1 pour des acidités libres $<4$ *N*, même pour les faibles concentrations.

TABLEAU II

PARTAGE DE Hf ENTRE UNE PHASE AQUEUSE NITRIQUE ET LE SOLVANT ACIDE[a]

| *Acidité N* | *g/l $q_a$ départ* | *Vol. $q_a$ à l'éq.* | *Vol. $q_s$ à l'éq.* | *g/l $q_a$ à l'éq* | *g/l $q_s$ à l'éq.* | *E %* | $\alpha_{Hf}$ |
|---|---|---|---|---|---|---|---|
| 4 | 5.5 | 10 | 10 | 4.82 | 0.74 | 13 | 0.15 |
| 4 | 16.5 | 10 | 10 | 15.1 | 0.77 | 4.7 | 0.05 |
| 4 | 27.5 | 10 | 10 | 26.4 | 0.74 | 2.7 | 0.028 |
| 5 | 0.275 | 10 | 10 | 0.100 | 0.175 | 63 | 1.75 |
| 5 | 0.550 | 10 | 10 | 0.265 | 0.285 | 51 | 1.08 |
| 5 | 1.10 | 10 | 10 | 0.570 | 0.530 | 48 | 0.93 |
| 5 | 1.27 | 10 | 10 | 0.930 | 0.34 | 26.8 | 0.36 |
| 5 | 2.2 | 10 | 10 | 1.72 | 0.48 | 21.8 | 0.27 |
| 5 | 2.6 | 10 | 10 | 2.02 | 0.58 | 22.1 | 0.29 |
| 5 | 5.5 | 10 | 10 | 4.92 | 0.58 | 10.5 | 0.18 |
| 5 | 6.4 | 10 | 10 | 5.5 | 1.0 | 15.6 | 0.18 |
| 5 | 11 | 10 | 10 | 9.58 | 1.48 | 13.5 | 0.15 |
| 5 | 13 | 10 | 10 | 11.2 | 1.8 | 13.7 | 0.16 |
| 5 | 22 | 10 | 10 | 19.3 | 2.8 | 13 | 0.14 |
| 5 | 38.5 | 10 | 10 | 34.8 | 3.85 | 10 | 0.11 |
| 6 | 0.275 | 10 | 10 | 0.050 | 0.225 | 81.5 | 4.4 |
| 6 | 0.550 | 10 | 10 | 0.150 | 0.400 | 72.7 | 2.67 |
| 6 | 1.10 | 10 | 10 | 0.400 | 0.700 | 63.5 | 1.75 |
| 6 | 1.09 | 10 | 10 | 0.535 | 0.555 | 51 | 1.04 |
| 6 | 2.2 | 10 | 10 | 1.28 | 0.92 | 41.7 | 0.72 |
| 6 | 2.24 | 10 | 10 | 1.2 | 1.0 | 44.6 | 0.83 |
| 6 | 5.5 | 10 | 10 | 3.68 | 1.82 | 33 | 0.51 |
| 6 | 5.6 | 10 | 10 | 3.6 | 2.0 | 35.7 | 0.55 |
| 6 | 11 | 10 | 10 | 7.12 | 3.9 | 35.2 | 0.55 |
| 6 | 22 | 10 | 10 | 15.6 | 6.4 | 29.4 | 0.41 |
| 6 | 44 | 10 | 10 | 33.8 | 10.2 | 23.2 | 0.3 |
| 7 | 5.5 | 10 | 10 | 1.58 | 3.92 | 71.2 | 2.48 |
| 7 | 11 | 10 | 10 | 3.84 | 7.2 | 65.5 | 1.85 |
| 7 | 22 | 10 | 10 | 9.6 | 12.4 | 56.3 | 1.29 |
| 7 | 55 | 10 | 10 | 32 | 23 | 41.8 | 0.72 |
| 8.5 | 5.5 | 10 | 10 | 0.2 | 5.3 | 96.5 | 26.5 |
| 8.5 | 11 | 10 | 10 | 0.64 | 10.3 | 94.5 | 16.2 |
| 8.5 | 22 | 10 | 10 | 1.9 | 20.1 | 91.5 | 10.6 |
| 8.5 | 38.5 | 10 | 10 | 7.3 | 31.2 | 81.3 | 4.3 |

[a] *cf.* Figs. 4 et 5

(*3*) Mais $\alpha_{Zr}$ restant également petit à ces acidités, le travail dans ces conditions ne serait pas économiquement rentable.

(*4*) Inversement, au dessus de 6 *N*, Zr et Hf s'extraient tous deux ($\alpha > 1$), la séparation serait donc mauvaise. C'est donc entre 5 et 6 *N* que doivent se trouver les meilleures conditions de travail.

Bien que par suite de l'interaction, il soit sans signification de calculer un coefficient de séparation $\beta = \alpha_{Zr}/\alpha_{Hf}$, nous ferons néanmoins le calcul pour évaluer, au moins

TABLEAU III

CALCUL DE $\beta$ AVEC LES DONNÉES DES TABLEAUX I ET II

| *Acidité N* | *Zr g/l départ* | *Hf g/l départ* | $\lambda_{Zr}$ | $\lambda_{Hf}$ | $\beta$ |
|---|---|---|---|---|---|
| 5 | 2.5 | 2.5 | 3 | 0.28 | 10.7 |
| 5 | 5 | 5 | 2.2 | 0.18 | 12.2 |
| 5 | 10 | 10 | 1.3 | 0.16 | 8.1 |
| 5 | 20 | 20 | 0.85 | 0.14 | 6.0 |
| 5 | 40 | 40 | 0.62 | 0.11 | 5.6 |
| 5 | 2.5 | 0.25 | 3 | 1.75 | 1.7 |
| 5 | 5 | 0.5 | 2.2 | 1.08 | 2.0 |
| 5 | 10 | 1 | 1.3 | 0.7 | 1.8 |
| 5 | 20 | 2 | 0.85 | 0.25 | 3.4 |
| 5 | 50 | 5 | 0.6 | 0.18 | 3.3 |
| 6 | 2.5 | 2.5 | 7.6 | 0.7 | 10 |
| 6 | 5 | 5 | 6.6 | 0.6 | 11 |
| 6 | 10 | 10 | 4.5 | 0.52 | 8.6 |
| 6 | 20 | 20 | 2.7 | 0.41 | 6.6 |
| 6 | 35 | 35 | 1.6 | 0.35 | 4.7 |
| 6 | 2.5 | 0.25 | 7.6 | 4.4 | 1.7 |
| 6 | 5 | 0.5 | 6.6 | 2.67 | 2.5 |
| 6 | 10 | 1.0 | 4.5 | 1.5 | 3.0 |
| 6 | 20 | 2.0 | 2.7 | 0.8 | 3.5 |
| 6 | 55 | 3.5 | 1.6 | 0.7 | 2.3 |

grossièrement, l'influence de l'acidité et pour mieux mettre en évidence l'importance de cette interaction que nous voulons étudier. Nous ferons ce calcul de deux manières également arbitraires: 1. Nous prendrons comme référence le $\lambda$ pour $|Zr| = |Hf|$. 2. Nous ferons le rapport $\beta$ pour $|Hf| = |Zr|/10$ (*cf.* Tableau III).

On voit que le calcul de $\beta$ est entaché d'une grosse imprécision dans la zône Hf < 1 g/l, ce qui est logique. Malgré cela, on constate que le facteur de séparation reste comparable, que le milieu soit 5 *N* ou 6 *N*. Pour des questions de rendement, il semble donc préférable de choisir le milieu 6 *N*. C'est dans ce milieu que nous étudierons l'interaction.

## *Étude de l'interaction Zr-Hf dans le processus d'extraction*

### *Influence de Zr sur l'extraction de Hf*

Pour cette étude, nous avons utilisé du hafnium marqué. Le dosage a été fait par comptage dans les deux phases. La somme zirconium plus hafnium a été ensuite dosée dans la phase aqueuse par voie chimique. Les résultats obtenus donnent une bonne évaluation de l'influence du zirconium sur Hf.

Les essais ont été faits dans trois domaines: 1. Sur un mélange initial contenant en poids 90% Zr et 10% Hf à des concentrations totales variant de 10 à 50 g/l, 2. Sur un mélange contenant 50% Zr et 50% Hf à des concentrations variant de 1 à 20 g/l, 3. Sur un mélange contenant 90% Hf et 10% Zr à des concentrations variant de 1 à 20 g/l. Ces concentrations correspondent, en gros, aux conditions expérimentales dans lesquelles nous pouvons nous trouver. Les résultats sont reportés sur le Tableau IV. La somme des comptages en phase solvant et en phase aqueuse donne une idée de la précision des mesures. Les différentes courbes de partage de Hf pour différents rapports Hf/Zr sont figurés sur les courbes Fig. 5.

On voit que pour des teneurs en Hf égales, la présence de Zr divise le facteur α par un coefficient 4 à 10 (dans le domaine où les rapports sont 10% Hf, 90% Zr).

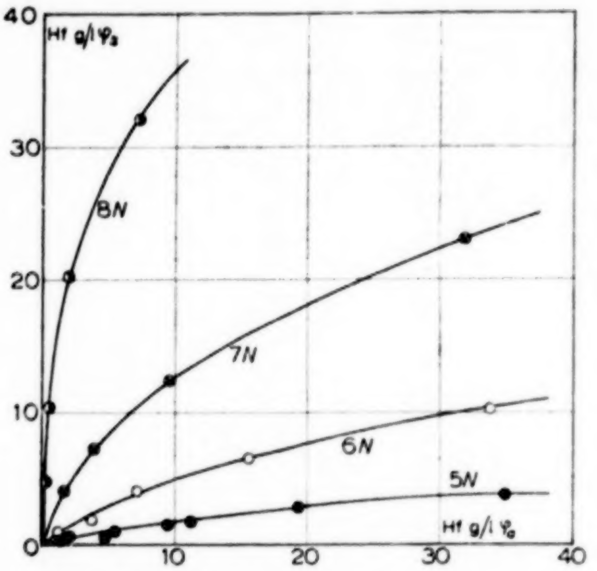

Fig. 4. Distribution de Hf à diverses concentrations en $HNO_3$.

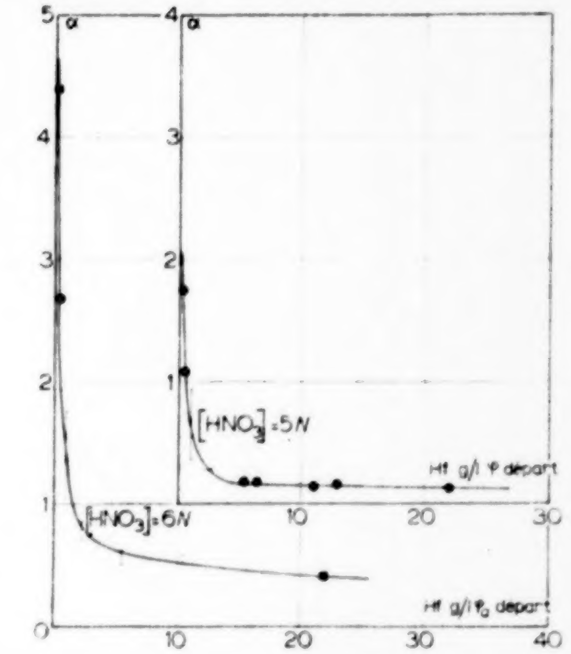

Fig. 5. Coefficient de partage $\alpha_{Hf}$.

TABLEAU IV

INFLUENCE DE Zr SUR L'EXTRACTION DE Hf

Solvant 60% TBP–40% WS, acide; milieu $HNO_3$ 6 *N*

| *Composition* | *Hf + Zr g/l départ* | *% Hf $\varphi_a$* | *% Hf $\varphi_s$* | $\frac{\varphi_a + \varphi_s}{\varphi_{ai}}$ % | $\alpha_{Hf}$ |
|---|---|---|---|---|---|
| 10% Hf<br>90% Zr | 10 | 71.5 | 28.3 | 99.8 | 0.39 |
| | 20 | 84.7 | 17.5 | 102.2 | 0.20 |
| | 35 | 87.5 | 11.4 | 98.9 | 0.13 |
| | 50 | 93.0 | 7.5 | 100.5 | 0.08 |
| 50% Hf<br>50% Zr | 1 | 45 | 55.1 | 100.1 | 1.22 |
| | 5 | 66 | 29.6 | 95.6 | 0.45 |
| | 15 | 80.5 | 25.0 | 105.5 | 0.31 |
| | 35 | 88.8 | 12.2 | 101.0 | 0.14 |
| 90% Hf<br>10% Zr | 1 | 40.6 | 57.0 | 97.6 | 1.4 |
| | 5 | 65.2 | 31.5 | 96.7 | 0.48 |
| | 10 | 78.5 | 25.8 | 104.3 | 0.33 |
| | 20 | 80.7 | 19.3 | 100 | 0.24 |
| 100% Hf | 1 | 36.5 | 63.5 | | 1.74 |
| | 5 | 56.0 | 44.0 | | 0.78 |
| | 11 | 64.8 | 35.2 | | 0.54 |
| | 22 | 76.6 | 29.4 | | 0.38 |

Comme on peut affirmer que, pour des teneurs de 50 à 90%, l'extraction du zirconium ne se trouve pas diminuée, au contraire*, on peut raisonnablement dresser un tableau des valeurs approximatives de $\beta$ dans les conditions de travail actuelles soit: % Hf variant de 0.1 à 15% d'une extrêmité à l'autre de l'extracteur (*cf.* Tableau V).

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* En effet on retrouve, dans le cas Hf et Zr, le cas du thorium et de l'uranium: le premier, qui s'extrait moins bien que le second, lui sert de relargant alors que son propre passage en phase solvant est inhibé.

Ce coefficient est en effet supérieur à celui que nous avons calculé en prenant les hypothèses les plus favorables.

On voit aussi qu'il se compare favorablement avec les coefficients de séparation des autres procédés de séparation: cristallisation du fluozirconate ($\beta \# 4$) et extraction du thiocyanate de zirconium par l'hexone ($4 < \beta < 5$).

TABLEAU V

COEFFICIENT DE SÉPARATION TENANT COMPTE DE L'INTERACTION Zr-Hf

| *Zr + Hf* g/l | $\beta$ |
|---|---|
| 1 | 6.6 |
| 2 | 10 |
| 5 | 10 |
| 10 | 11.4 |
| 20 | 12.9 |
| 35 | 12.6 |

## REMERCIEMENTS

Nous tenons à exprimer nos remerciements à Mme PILLARD du Service de Physique Mathématique qui a calculé l'équation de la courbe d'extraction du zirconium.

## RÉSUMÉ

On a examiné l'importance de divers facteurs influençant l'extraction par le tributylphosphate du zirconium en quantités pondérales et sa séparation du hafnium.

## SUMMARY

Factors influencing the extraction of macro amounts of zirconium by tributylphosphate and this separation of zirconium from hafnium are discussed.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten des Zirkoniums und seine Trennung von Hafnium bei der Extraktion mit Tributylphosphat.

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# A PROCEDURE FOR THE DETERMINATION OF THE RARE EARTH ELEMENTS, LANTHANUM THROUGH LUTETIUM, IN CHONDRITIC, ACHONDRITIC AND IRON METEORITES BY NEUTRON-ACTIVATION ANALYSIS

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(Received November 21th, 1960)

## INTRODUCTION

A knowledge of the relative abundances of the elements is important in the formulation of a theory of nucleosynthesis[1-3]. SUESS AND UREY[3] have critically examined compilations of atomic abundances, and CAMERON[2] has published a revised table of the relative abundances of nuclides.

The abundances of the rare earths have been measured by NODDACK[4] by X-ray spectroscopy on two silicate meteoritic samples (one a composite of eight silicate meteorites and the other a composite of fourteen) and on a composite of seven iron meteorites. MINAMI[5] made similar X-ray spectroscopic analyses on four different sediments.

The most serious disagreement between the two investigations is that the abundances of the light rare earths are shown to be about eight times greater in the sediments than in the meteorites.

Neutron-activation analysis combined with an ion-exchange separation of the rare earths provides a powerful new tool for accurately determining the abundances of the rare earths. The principal advantages of the neutron-activation technique are (*1*) that it allows determinations of abundances in the parts per million to fractional parts per billion range and (*2*) that there is freedom from contamination because the chemical processes follow the neutron irradiation. The chief disadvantage, namely, the necessity of handling extremely radioactive materials, is obviated by shielding and remote manipulation.

Neutron-activation analysis has been discussed by several authors[6-9]. The determination of the abundances of uranium in stone meteorites by HAMAGUCHI, REED AND TURKEVICH[10], of thorium in iron meteorites by BATE, POTRATZ AND HUIZENGA[11], and of bismuth, thallium, and mercury in stone meteorites by EHMANN AND HUIZENGA[12] has adequately demonstrated the feasibility and reliability of the neutron-activation technique.

A procedure for the determination of individual rare earths in graphite employing neutron activation and ion exchange separation of the rare earths has been described by CORNISH[13].

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An unpublished procedure developed by R. SCHMITT AND A. MOSEN for the determination of high-cross-section rare earths in reactor-grade zirconium was modified for application to samples of chondritic, achondritic, and iron meteorites. This paper describes in detail the radiochemical procedure used in the successful analysis of the meteorites Allegan, Richardton, Nuevo Laredo, Pasamonte, and Odessa. The results of some of these analyses have been reported elsewhere[14]. The procedure should also be applicable to the analysis of terrestrial stones and sediments.

## REAGENTS AND APPARATUS

### *Solutions of rare earth standards*

Solutions containing about 0.5 mg/ml of the rare earth element are prepared by dissolving suitable compounds in HCl and diluting with deionized distilled water. In the meteorite analyses reported here, Johnson-Matthey spectrographic-standard quality oxides of Sc, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu were used. Oxides of lanthanum and terbium were obtained from Spex Industries and from Research Chemicals, respectively. The cerium standard was prepared from G. F. Smith Chemical Company $(NH_4)_2Ce(NO_3)_6$ (99.99% pure). Other cerium compounds were found to be unacceptable because of lanthanum contamination. The G. F. Smith cerium standard was found to contain 0.021 lanthanum atoms per 100 cerium atoms. Small amounts of lanthanum will cause difficulty in the activation analysis, because the induced $^{140}$La activity in the cerium standards will swamp the induced $^{143}$Ce activity. The standard rare-earth solutions are also used as rare-earth carrier solutions. Promethium carrier is added in the form of a 2.6-yr $^{147}$Pm tracer, which is a pure $\beta$-emitter.

### *β,β-Dichlorodiethyl ether*

Bis(2-chloroethyl)ether, Eastman No. 866, is prepared for use by passing it through a column of neutral alumina, 100 to 200 mesh (Bio-Rad AG-7, Bio-Rad Laboratories, Richmond, California).

### *Ion-exchange column*

The apparatus and ion-exchange procedures used to separate the individual rare earths are essentially those of NERVIK[15]. The column is 60 cm long by 0.6 cm in diameter, and is packed with Dowex 50W-X12, minus-400 mesh, ion-exchange resin. This resin (specially prepared by Bio-Rad Laboratories) has a settling rate of 0.5 to 2.0 cm/min. The resin is washed three times with deionized distilled water, and then is washed twice with 1 *M* ammonium lactate, pH 3.2. Before the resin is put into the column, it is boiled and stirred in 1 *M* ammonium lactate, pH 3.2, to remove gases (the resin-to-solution ratio is about 3). The rare earths are eluted with 1 *M* ammonium lactate, whose initial pH of 3.2 is changed at the rate of approximately 0.1 pH unit per hour. This is accomplished by having a 1 *M* ammonium lactate solution, pH 7, dilute the initial pH 3.2 solution at about 1 drop every 10 sec. The solutions are mixed by a magnetic stirrer. The column is heated by a water jacket, which is maintained at about 80° by heating tape. A pressure of about 5 lb/in.$^2$ of $N_2$ gas is kept over the solutions and is maintained by an ordinary pressure regulator. The column effluent is caught in 10-mm by 100-mm test tubes, using a Packard ion-exchange turntable set to collect 10 drops per tube.

## PROCEDURE

### *Separation of rare earths from meteoritic matrices*

#### *Irradiation*

Samples (about 5 g) of the meteorite to be analyzed are prepared for irradiation in one of two ways. Stony (chondritic or achondritic) samples are crushed in a hardened-steel diamond mortar that is reserved for such analyses to avoid contamination. Iron samples are etched with rare-earth-free 6 *N* hydrochloric acid. If the stony specimen is etched with hydrochloric acid, as much as 20% of the rare earths may be leached away, presumably through the dissolution of the sulfide phase (in some chondrites this phase is concentrated in veins). The sample is then weighed on an analytical balance and transferred to a clean polyethylene vial.

The sample and the fourteen rare earth standards are irradiated simultaneously in the General Atomic TRIGA reactor in a flux of about $2 \cdot 10^{12}$ thermal neutrons/cm$^2$/sec for 2 h. The meteorite sample and the standards are placed in separate containers in the rotary specimen rack of the TRIGA reactor. This rack is continuously rotated at 1 rev./min during irradiation, so that all specimens are exposed to the same neutron flux. The amounts in $\mu$g of the irradiated rare-earth standards and scandium are: La, 60; Ce, 380; Pr, 70; Nd, 60; Sm, 6; Eu, 3; Gd, 9; Tb, 80; Dy, 80; Ho, 8; Er, 50; Tm, 50; Yb, 5; Lu, 5 and Sc, 50.

The radioactivities induced in the rare earths of a chondritic meteorite and the sensitivities for each of the rare earths are summarized in Table I.

#### *Initial separation steps for stony meteorites*

After the sample has been irradiated, the polyethylene sample tube and vial are opened with a special tool. The tube is handled with 4-ft. tongs, and the chemistry is carried out in a filtered hood behind a 4-in.-thick lead shield. Rare earth carriers are added to the sample in the form of oxides prior to the fusion step, described below. The carriers are prepared in the following manner. Exactly 1.00 ml (0.5 mg) of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 2.00 ml of the $^{147}$Pm tracer carrier are pipetted into a 100-ml beaker. The hydroxides are precipitated with ammonium hydroxide that has been prepared by bubbling ammonia into a polyethylene bottle of deionized, distilled water. After the addition of paper pulp, the solution is filtered on a Whatman No. 42 filter paper and all the precipitate is transferred from the beaker. Dilute ammonia solution is used for the wash solution. The filter paper is placed in an 80-ml zirconium crucible (obtained from Oregon Metallurgical Corporation, Albany, Oregon) that is used to fuse the sample. The crucible is covered and heated gently to dry the paper. The heat is gradually increased to char the paper and, finally, the full heat of a Meker burner is applied. This ignition must be carried out carefully to avoid loss of carrier.

To fuse a 5-g sample, 25 g of sodium peroxide is used. About half of the peroxide is poured into the crucible on top of the carriers. The sample is then added, followed by the remainder of the peroxide. The mixture is then carefully stirred with a glass rod using care not to disturb the carriers on the bottom of the crucible.

The crucible is held with a pair of 4-ft. tongs in the flame of a Meker burner until the mixture is completely molten. The heating is continued for at least five more minutes to ensure complete fusion of the sample and complete exchange of the carriers with the rare earths. This step is very critical.

## TABLE I

### RARE EARTH RADIOACTIVITIES IN METEORITES AFTER NEUTRON ACTIVATION[a]

| *Element* | *Neutron-capture reaction*[b] | *Isotopic abundance*[c] (%) | *Half life* | *Activity 24 h after irradiation*[d] (counts/min) | *Elemental abundance*[e] (p.p.m.) | *Sensitivity for 1-g sample*[f] (p.p.m.) |
|---|---|---|---|---|---|---|
| $_{57}$La | $^{139}\mathrm{La}(n,\gamma)^{140}\underline{\mathrm{La}}$ | 99.9 | 40 h | $2\cdot10^{4}$ | 0.33 | 0.002 |
| $_{58}$Ce | $^{140}\mathrm{Ce}(n,\gamma)^{141}\underline{\mathrm{Ce}}$ | 88.5 | 32 day | $2\cdot10^{2}$ | — | — |
| | $^{142}\mathrm{Ce}(n,\gamma)^{143}\underline{\mathrm{Ce}}$ | 11.1 | 33 h | $1\cdot10^{3}$ | 0.51 | 0.05 |
| $_{59}$Pr | $^{141}\mathrm{Pr}(n,\gamma)^{142}\underline{\mathrm{Pr}}$ | 100 | 19 h | $1\cdot10^{3}$ | 0.12 | 0.01 |
| $_{60}$Nd | $^{146}\mathrm{Nd}(n,\gamma)^{147}\underline{\mathrm{Nd}}$ | 17.2 | 11.6 day | $3\cdot10^{2}$ | 0.63 | 0.2 |
| | $^{148}\mathrm{Nd}(n,\gamma)^{149}\mathrm{Nd}$ | 5.7 | — | — | — | — |
| | 1.8-h $^{149}\mathrm{Nd} \rightarrow {}^{149}\underline{\mathrm{Pm}}$ | | 50 h | $\sim1\cdot10^{2}$ | — | — |
| | $^{150}\mathrm{Nd}(n,\gamma)^{151}\mathrm{Nd}$ | 5.6 | — | — | — | — |
| | 12-min $^{151}\mathrm{Nd} \rightarrow {}^{151}\underline{\mathrm{Pm}}$ | | 27.5 h | $\sim2\cdot10^{2}$ | — | — |
| $_{62}$Sm | $^{152}\mathrm{Sm}(n,\gamma)^{153}\underline{\mathrm{Sm}}$ | 26.8 | 47 h[g] | $1\cdot10^{5}$ | 0.22 | 0.00002[h] |
| $_{63}$Eu | $^{151}\mathrm{Eu}(n,\gamma)^{152}\underline{\mathrm{Eu}}^{m}$ | 47.8 | 9.2 h | $4\cdot10^{5}$ | 0.083 | 0.000001[h] |
| | $^{151}\mathrm{Eu}(n,\gamma)^{152}\underline{\mathrm{Eu}}$ | 47.8 | 12.5 yr | $1\cdot10^{3}$ | — | — |
| $_{64}$Gd | $^{158}\mathrm{Gd}(n,\gamma)^{159}\underline{\mathrm{Gd}}$ | 24.9 | 18 h | $2\cdot10^{3}$ | 0.34 | 0.02 |
| | $^{160}\mathrm{Gd}(n,\gamma)^{161}\mathrm{Gd}$ | 21.9 | — | — | — | — |
| | 3.7-min $^{161}\mathrm{Gd} \rightarrow {}^{161}\underline{\mathrm{Tb}}$ | | 7.0 day | $3\cdot10^{2}$ | — | — |
| $_{65}$Tb | $^{159}\mathrm{Tb}(n,\gamma)^{160}\underline{\mathrm{Tb}}$ | 100 | 72 day | $4\cdot10^{2}$ | 0.051 | 0.01 |
| $_{66}$Dy | $^{164}\mathrm{Dy}(n,\gamma)^{165}\underline{\mathrm{Dy}}$ | 28.2 | 2.3 h | $6\cdot10^{3}$ | 0.37 | 0.006 |
| $_{67}$Ho | $^{165}\mathrm{Ho}(n,\gamma)^{166}\underline{\mathrm{Ho}}$ | 100 | 27.2 h | $2\cdot10^{4}$ | 0.075 | 0.00002[h] |
| $_{68}$Er | $^{168}\mathrm{Er}(n,\gamma)^{169}\underline{\mathrm{Er}}$ | 27.1 | 9.4 day | 70 | — | — |
| | $^{170}\mathrm{Er}(n,\gamma)^{171}\underline{\mathrm{Er}}$ | 14.9 | 7.5 h | $3\cdot10^{3}$ | 0.21 | 0.007 |
| $_{69}$Tm | $^{169}\mathrm{Tm}(n,\gamma)^{170}\underline{\mathrm{Tm}}$ | 100 | 129 day | 300 | 0.038 | 0.01 |
| $_{70}$Yb | $^{168}\mathrm{Yb}(n,\gamma)^{169}\underline{\mathrm{Yb}}$ | 0.14 | 32 day | $8\cdot10^{2}$ | — | — |
| | $^{174}\mathrm{Yb}(n,\gamma)^{175}\underline{\mathrm{Yb}}$ | 31.8 | 4.2 day | $4\cdot10^{3}$ | 0.19 | 0.005 |
| $_{71}$Lu | $^{175}\mathrm{Lu}(n,\gamma)^{176}\underline{\mathrm{Lu}}$ | 97.4 | 3.7 h | $4\cdot10^{2}$ | — | — |
| | $^{176}\mathrm{Lu}(n,\gamma)^{177}\underline{\mathrm{Lu}}$ | 2.62 | 6.8 day | $2\cdot10^{3}$ | 0.036 | 0.002 |

[a] Neutron-induced rare-earth activities in 5-g chondritic meteorite irradiated at 300 kw for 2 h, *i.e.*, at a thermal flux of $2\cdot10^{12}$ neutrons/cm²/sec in the TRIGA reactor.

[b] Abundances of stable isotopes are determined from the activity of radioisotopes, underscored once.

[c] Isotopic percentage of the stable isotopes that undergo neutron capture.

[d] The activity observed 24 h after irradiation is expressed in integral counts per min and is uncorrected for chemistry yield. All $\gamma$-rays greater than 20 keV, emitted by the rare earths in the combined two or three test tubes of the peaks, were measured by a 1–3/4 in. by 2 in. NaI(Tl) well-type scintillation spectrometer. Exceptions were 18-h $^{159}$Gd, which was window-counted between 20 and 120 keV; 9.4-day $^{169}$Er and 129-day $^{170}$Tm, which were $\beta$-counted; and 32-day $^{141}$Ce, which should be window-counted between 100 and 180 keV.

[e] Elemental abundances of natural elements were calculated by assuming terrestrial and meteoritic isotopic abundances to be identical. The four rare earth isotopic ratios observed in Allegan and Richardton have checked the validity of the above assumption[14]. Units are expressed in parts per million by weight. Abundances are averaged for the meteorites Allegan and Richardton.

[f] Sensitivities in parts per million for determination of elemental abundances are given for a thermal-neutron flux of $2\cdot10^{12}$ neutrons/cm²/sec and an irradiation of 2 h. The sensitivity is based on a minimum of 20 integral or window $\gamma$-ray counts per minute 24 h after irradiation. A chemical yield of 50% is assumed.

[g] A half life of 46 h was observed for $^{153}$Sm.

[h] Sensitivities in parts per million are based on a minimum of 20 $\beta$-counts per min 24 h after irradiation.

When the melt has cooled, the uncovered crucible is placed on its side in an 800- or 1000-ml beaker. To dissolve the melt, 150 ml of 6 *N* hydrochloric acid are poured into the beaker in small increments. The reaction is vigorous. After the melt has dissolved, the crucible is removed from the beaker and rinsed with deionized, distilled water. The rinsings are added to the sample solution. The beaker is placed on a hot plate and heated to decompose the peroxides. A boiling tube is placed in the beaker to prevent bumping. Some silica is precipitated at this point, and the solution is centrifuged in 90-ml centrifuge tubes to remove the silica. The centrifuge is shielded with 4 in. of lead.

The solution is decanted into an 800-ml beaker, and an equal volume of ethyl alcohol is added. The beaker is placed in an ice bath, and a stream of hydrogen chloride gas (from a cylinder) is bubbled through the solution for 1 to 2 h to precipitate sodium chloride. Ice is added to the bath as needed. The solution is centrifuged in 90-ml glass tubes to remove the sodium chloride, the tubes being handled with tongs. The solution is then decanted into an 800-ml beaker.

The solution is now boiled to reduce its volume by half. This removes most of the alcohol and precipitates a large amount of silica, which is removed by centrifuging. The solution is decanted into a 500-ml open-top separatory funnel, and iron is extracted from the solution using $\beta,\beta$-dichlorodiethyl ether. The ether and solution are mixed with a three-bladed polyethylene stirrer driven by a small, variable-speed electric motor. It is advisable to avoid turbulent stirring, since suspensions may result. The ether is added in two or three portions. Usually, the ether from the second extraction shows only a faint coloration from the iron (further steps are described below in *Further procedure for both stony and iron meteorites*).

### *Initial separation steps for iron meteoritic matrices*

After the iron meteorite has been dissolved in 150 ml of hot 6 *N* hydrochloric acid by moderate heating on a hot plate, about 10 ml of 30% hydrogen peroxide is added to oxidize the iron to the tervalent state. Rare-earth carriers, in amounts given in the procedure for separation of rare earths from a stony meteoritic matrix, are added to the beaker containing the iron and 6 *N* hydrochloric acid immediately before dissolution begins. The solution is heated to decompose excess hydrogen peroxide and centrifuged to separate small amounts of insoluble matter. To the solution, an equal volume of concentrated hydrochloric acid is added to bring the HCl normality to about eight.

The solution is transferred to a large separatory funnel. About nine iron extractions are performed, using 50-ml portions of $\beta,\beta$-dichlorodiethyl ether. Again, the ether and solution are stirred with a three-bladed polyethylene stirrer driven by a small, variable-speed electric motor, and turbulent stirring is avoided. The final green aqueous solution is attributed to the nickel chloride ion.

After the iron extractions, the aqueous solution is transferred to a large beaker and the solution is heated to drive off any dissolved ether.

### *Further procedure for both stony and iron meteorites*

The aqueous solution is transferred to a 600-ml beaker, and ammonia is bubbled into the solution to precipitate the hydroxides of the rare earths and zirconium. Three lecture bottles of ammonia are used simultaneously to speed the precipitation.

Since the solution is very acidic, it takes a considerable amount of ammonia to neutralize it and precipitate the hydroxides. Before centrifuging, hot water should be added to dissolve any ammonium chloride that may form. The solution is centrifuged in a 90-ml glass tube, so that all of the hydroxide precipitate is collected directly in one tube. The solution is discarded in a "hot waste" bottle.

The precipitate is dissolved by adding about 5 ml of concentrated hydrochloric acid to the centrifuge tube and stirring. This solution is diluted with 10–20 ml of water, and any insoluble material is centrifuged. It may be necessary to repeat the HCl dissolution step. The hydroxides are precipitated with ammonia. An excess of ammonia is used to complex any nickel that may be present. The solution is centrifuged, and after the supernatant liquid is discarded the precipitate is dissolved with about 1 ml of concentrated hydrochloric acid. This solution is transferred drop by drop to a small polyethylene centrifuge tube containing 3 ml of 48% hydrofluoric acid in order to precipitate the rare-earth fluorides. The solution is centrifuged, and the supernate, which contains about 80–90% of the scandium, is decanted into a centrifuge tube labeled "Sc" to be saved for the scandium procedure. Since scandium forms a complex ion, $ScF_4^-$, only a small fraction (20%) of the scandium is coprecipitated with the rare earth fluorides. The rare earth fluorides are dissolved with 2 ml of saturated boric acid and 1 ml of concentrated nitric acid. The solution is diluted to 10 ml and the rare earth hydroxides are precipitated with ammonia. The solution is centrifuged and the supernate is discarded. The precipitate is dissolved in 1 ml of 6 *N* hydrochloric acid and then diluted to 10 ml. The solution is transferred a drop at a time into a tube containing 3 ml of 48% hydrofluoric acid (scandium holdback carrier should not be added, since this leads to interference with the ion-exchange separation). The solution is centrifuged and the supernate is discarded. The rare earth fluorides are dissolved with 2 ml of boric acid and 1 ml of concentrated nitric acid and diluted to 10 ml. Concentrated ammonia solution is used to precipitate the hydroxides, and the supernate is discarded after the solution is centrifuged. The precipitate is dissolved in 1 ml of hydrochloric acid and is then diluted to 10 ml. The rare earths are decontaminated of scandium twice more by repeating the rare earth fluoride precipitation and boric acid dissolution steps described above. After the final boric acid dissolution, the hydroxides are reprecipitated with ammonia.

After being centrifuged, the precipitate is dissolved with hydrochloric acid and again precipitated with ammonia. This solution is centrifuged, and the remaining solution is decanted. 5 ml of 6 *N* hydrochloric acid is added to dissolve the precipitate. The solution is transferred to a 500-ml separatory funnel and diluted to 25 ml. Ice chips (of demineralized, distilled water) are added to cool the solution to approximately 0°. About 2 g of ammonium thiocyanate is added, followed by 100 ml of diethyl ether. The flask is shaken and the aqueous layer drawn off. The ether layer is discarded. This extraction is repeated until the ether layer shows only a slight pink coloration from the iron thiocyanate complex. Cobalt is also removed by this extraction.

The solution is boiled to remove ether and carbon dioxide, and it is then transferred to a glass centrifuge tube, where a series of three ammonia precipitations is carried out. The hydroxides are dissolved in 1 ml of concentrated hydrochloric acid and diluted to 10 ml with water before precipitation with ammonia. After the final ammonia precipitation, the hydroxides are dissolved in 2 ml of concentrated hydrochloric acid.

This is poured into a prepared ion-exchange column. The concentrated-HCl form of Bio-Rad Dowex-2, 100- to 200-mesh resin, is used in a column about 0.6 cm in diameter by 10 cm long. The anion exchange resin is prepared by passing 10 ml of concentrated hydrochloric acid through the column before the rare earth solution. The rare earths pass through the column, and elements such as iron, which form complex anions in concentrated hydrochloric acid, are held in the column. When the liquid meniscus reaches the resin, 2.5 ml of concentrated hydrochloric acid is added. This is eluted until the liquid meniscus again reaches the resin.

The rare earth hydroxides are once again precipitated from the column eluant with ammonia gas. Water is added to dissolve the ammonium chloride which precipitates with the hydroxides. After being centrifuged, the hydroxides are dissolved in the minimum amount of 6 *N* hydrochloric acid, diluted with 10 ml of water, and reprecipitated with ammonia. The solution is centrifuged, and the supernate is decanted. The rare earths are now ready to be dissolved and passed through a Dowex 50W-X12, minus-400 mesh ion-exchange column to separate them from one another.

### *Ion-exchange separation of rare earths*

The precipitate of rare earth hydroxides is dissolved with a minimum amount of dilute hydrochloric acid and is diluted with 10 ml of water. About 0.5 ml of Dowex 50W-X12, minus-400 mesh ,cation resin (about 2 ml of neutral resin mixture of which about 0.5 ml is resin) is added. The solution is heated to boiling, stirred, centrifuged, and decanted. While being stirred, the resin is washed with about 10 ml of hot water, centrifuged, and decanted. While being stirred, about 2 ml of water is added to the resin, and the gases are boiled off. Before transferring the 0.5 ml of resin, which contains the adsorbed and activated rare earths, to the top of the ion-exchange column, 1 *M* ammonium lactate (pH 3.2) is run through the column until the effluent has a constant pH of 3.2 (this equilibration may take as long as 12 h). The rare earths are eluted at about 3 drops/min, or 0.5 ml/cm$^2$/min, and 10 drops are collected in each test tube.

### *Preparation of scandium for counting*

To the contents of the tube labeled "Sc", about 3 mg of praseodymium carrier and 6 ml of concentrated perchloric acid are added. After being heated for some time (5 min to a day) on a steam bath and cooled, the solution is centrifuged and decanted. The $PrF_3$ and $ScF_3$ are dissolved in 2 ml of saturated boric acid and 1 ml of concentrated nitric acid. After dilution to 10 ml, concentrated ammonia solution is added to the solution to precipitate the hydroxides. The solution is centrifuged and decanted.

The hydroxides are dissolved in 2 ml of concentrated hydrochloric acid and are poured into a prepared ion-exchange column. The concentrated-HCl form of Bio-Rad Dowex-2, 100- to 200-mesh resin, is used in a column about 0.6 cm in diameter and 10 cm long. The anion resin is prepared by passing 10 ml of concentrated hydrochloric acid through the column before the addition of the scandium–praseodymium solution. The scandium–praseodymium ions pass through the column. When the liquid reaches the top of the column, 2 ml of concentrated hydrochloric acid is added. This is eluted until the liquid level reaches the top of the column.

The scandium and praseodymium hydroxides from the column eluant are precipitated with ammonia gas and centrifuged. After the supernate has been decanted, the precipitate is dissolved in the minimum amount of 3 *N* nitric acid, transferred to a culture tube, and diluted to the same volume as the scandium standard that was irradiated simultaneously with the specimen. The 85-day $^{46}$Sc is counted integrally above 750 keV for low counting rates or is window-counted for the $^{46}$Sc 0.89-MeV $\gamma$-ray in a standard scintillation spectrometer with a NaI(Tl) crystal.

*Radioactivity measurements of the rare earths*

Each of the test tubes containing 10 drops of effluent is placed in a well-type scintillation spectrometer with a 1-3/4 in. by 2 in. NaI(Tl) crystal, and all $\gamma$-rays corresponding to pulses greater than 20 keV are integrally counted. Almost all of the neutron-activated rare earth elements decay by negatron emission, accompanied by hard $\gamma$-ray emission; thus, they lend themselves to $\gamma$-ray spectroscopy. A plot of the integral counting rate *versus* the number of the test tube containing the effluent is given in Fig. 1, where it may be observed that the rare earths elute in the order of their decreasing atomic numbers. In order to ascertain the order of elution and to identify unequivocally the elution peaks, the effluents in the two or three test tubes making up each peak (or shoulder near a peak, as in the case of gadolinium) are combined into a single, standard-size culture tube. A $\gamma$-ray spectrum of the activated rare earth is taken with a 256-channel analyzer coupled to a well-type 1-3/4 in. by 2 in. NaI(Tl) crystal. For comparison, $\gamma$ spectra of each of the fourteen rare earth standards are also obtained with the multichannel analyzer.

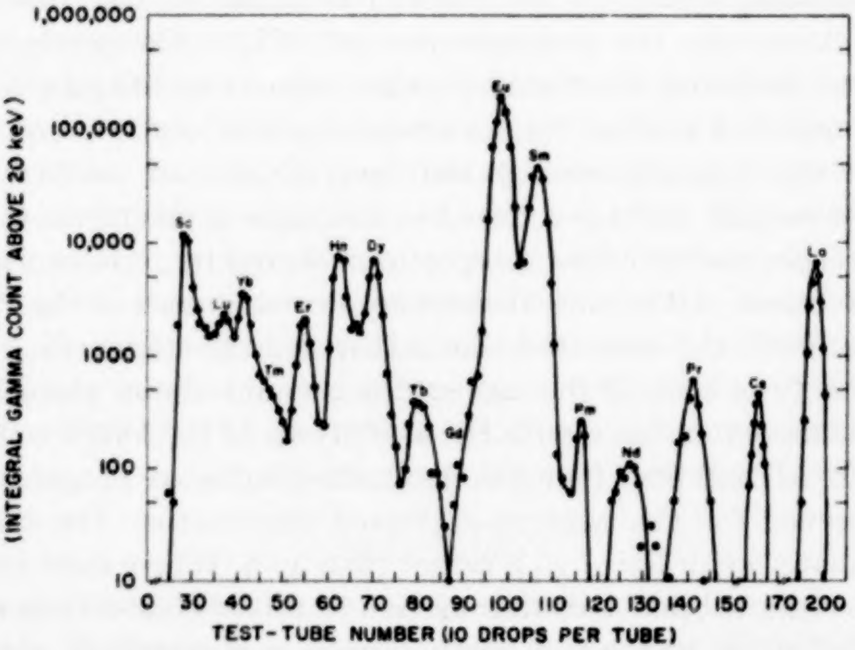

Fig. 1. Ion-exchange separation of rare earths from the Allegan meteorite Ion-exchange resin: Dowex AG50W-X12, minus 400 mesh, 0.5–2.0 cm/min; settling rate, according to Livermore specifications (processed by Bio-Rad Company). Column: 0.5 cm in diameter by 60 cm long; column temperature: 80°; flow rate of eluant: 0.5 ml/cm$^2$/min; gradient elution: 0.08 pH unit change per h. Rare-earth activities induced in 5.1 g of Allegan meteorite exposed to $\sim 10^{16}$NVT.

After identification of the rare earths by $\gamma$-ray spectra and elution position, the culture tubes are placed in alternate positions in the circular indexing rack of an automatically operated, well-type scintillation spectrometer (Packard Autogamma) with a 1-3/4 in. by 2 in. NaI(Tl) crystal. The irradiated rare earth standards (in solution) are also transferred to culture tubes and placed in alternate positions in the automatic spectrometer. Specifically, each rare earth standard is placed adjacent to its column-separated rare earth counterpart. To ensure identical counting geometries, the volume of rare earth standard in each culture tube is identical to the volume of rare earth from the meteoritic source. Furthermore, a $^{137}$Cs standard $\gamma$-ray source and culture tubes containing pure water (the same volume as in the activated-rare-earth tubes) are placed at uniform points in the rack in order to check any drift in the scintillation spectrometer and to count the background at regular intervals. All tubes are counted for a preset time or for a preset total count of $10^6$, whichever occurs first.

It is necessary to count only two of the separated rare earths and their respective standards — 9.4-day $^{169}$Er and 129-day $^{170}$Tm — by $\beta$-counting methods. After the $\gamma$ radioactivity of 7.5-h $^{171}$Er has been measured, a definite amount of praseodymium carrier (10 mg) is added to the erbium effluent (part of the erbium effluent before the addition of praseodymium carrier should be kept for activation analysis) and to the erbium standard, which are transferred to separate test tubes. An identical procedure is followed for the determination of $^{170}$Tm. The precipitates of praseodymium oxalate, prepared by standard radiochemical techniques, are filtered onto paper disks, mounted on 1/16-in.-thick aluminum plates, and covered with 0.00025 in. of Mylar. Since the praseodymium oxalate precipitates are uniformly thick and of nearly the same weight, and are counted in the same geometry in the Geiger region of a Sugarman-type, methane-flow, proportional $\beta$-counter, it is unnecessary to apply $\beta$-counting corrections. Aluminum absorption measurements of the $^{169}$Er and $^{170}$Tm $\beta$'s are taken for both the separated rare earths and the standards.

The radioactivity of each of the rare earths is counted and plotted for a decay of usually three or more half lives, with the exceptions of the long-lived 129-day $^{170}$Tm and 85-day $^{46}$Sc. All half lives found in the decay graphs are in agreement with those previously observed for the neutron-activated rare earths. The only exception is $^{153}$Sm, which shows a half life of 46 h rather than 47 h. Where sufficient radioactivity is present, it is estimated that decontamination factors of greater than $10^4$ are achieved.

Radiochemical yields of the rare earth carriers and scandium are ascertained by comparing the activities resulting from neutron-activation analysis of the decayed carriers with the neutron-induced activities of a known amount of the individual rare earth standards. In some cases, it is desirable to follow the decay of the rare earth for long periods of time; consequently, their chemical yields are determined by neutron-activation analysis on known aliquots of the partially decayed carriers. After the decay of promethium activity resulting from the decay of neodymium precursors, 2.6-yr $^{147}$Pm atoms are coprecipitated with praseodymium oxalate, and $^{147}$Pm is $\beta$-counted to determine the promethium chemical yield. For all rare earths, during chemical-yield determinations the induced activities in the carriers are at least 100 times greater than the residual activity from the meteorite activation. Yields of about 25% to 50% are obtained.

In addition to the neutron-induced rare earth activities in the rare earth carriers during chemical-yield determinations, an appreciable amount of 15-h $^{24}$Na activity is produced. This $^{24}$Na activity is particularly troublesome for Pr, Gd, Ho and Er, since the half lives for these elements are comparable to that of $^{24}$Na. To subtract the

$^{24}$Na activity from the total activities of $^{24}$Na and rare earths, the $\gamma$-rays of the respective rare earths and of a separate $^{24}$Na source are both measured at two $\gamma$-ray energy settings of the scintillation spectrometer; one corresponds to the rare earth $\gamma$-ray energy (usually a low-energy $\gamma$ ray), and the other setting detects only the highly energetic 2.75-MeV $\gamma$ ray of $^{24}$Na.

When the 2.75-MeV $\gamma$ ray counting rate of the $^{24}$Na source is normalized to the counting rate of the 2.75-MeV $\gamma$ ray in the rare-earth carrier, the contribution of the $^{24}$Na counting rate to the total is easily calculated and subtracted. For the worst cases, as much as 30% of the total radioactivity may be from 15-h $^{24}$Na.

If the activity level of the $^{24}$Na is too high, it is helpful to separate sodium from the rare earth lactate solution before the neutron-activation analyses are made. Separation of sodium is easily performed by repeated ammonium hydroxide precipitations ($NH_3$ gas is used) of the rare earths. In order to coprecipitate the individual rare earths, which are present in about 0.2- to 0.3-mg quantities, a few milligrams of ferric carrier (Johnson and Matthey, spectrographic grade) is added to the rare earth lactate solution. After the rare earth lactate solution has been made ammoniacal by ammonia gas, the hydroxide precipitates when the lactate complex has been oxidized by the addition of 1 ml of 30% hydrogen peroxide.

After the values for the rare earth activities have been corrected for chemical yield, the elemental abundances of the rare earths are determined by comparing the radioactivity of each eluted rare earth with the specific activity of the corresponding rare earth radioisotope. All comparisons of activities must be made an equal time after the neutron irradiation has ended. In the analyses performed by the authors to calculate the elemental abundances of the rare earths, it was assumed that the isotopic abundances of meteoritic and terrestrial rare earths would be identical. During this work, the abundance ratios for the isotope pairs $^{140}$Ce/$^{142}$Ce, $^{146}$Nd/$^{150}$Nd, $^{158}$Gd/$^{160}$Gd, $^{168}$Er/$^{170}$Er, $^{168}$Yb/$^{174}$Yb and $^{175}$Lu/$^{176}$Lu were measured, and the ratios were, indeed, found to be the same for both meteoritic and terrestrial rare earths.

## DISCUSSION

The neutron intensities and spectra must be nearly identical throughout the specimen and the standards. Particularly in a large specimen, *e.g.*, one of *ca.* 5–10 g of low- and medium-mass constituency, it is possible that the specimen might behave as a moderator, thereby increasing the thermal-neutron flux in the specimen relative to that in the standards. On the other hand, the specimen could act as a thermal and/or epithermal neutron sink and decrease the neutron flux available for activation of the rare earths throughout the specimen. The absorption and scattering cross sections for the constituents of a typical 5-g chondritic and 10-g iron meteorite indicate that, compared with standards that are very thin to neutron absorption, differences of about 1% and 7% in the neutron intensities and spectra are expected from the combined effects of absorption and scattering in stony and iron meteorites, respectively.

In order to test the absorption and scattering effects of meteoritic specimens experimentally, an extreme method was chosen. Thin sources of each rare earth (thin to *ca.* 1% of thermal-neutron absorption in most cases) were prepared. The thin sources were individually placed in the center of separate chondritic mockup specimens and in the center of iron bars 1.27 cm in diameter and 1.27 cm long. Both the mockups and the rare earth standard sources were simultaneously irradiated in separate containers in the circular rotating rack of the TRIGA reactor. The radioactivities of the thin sources were then measured. The results are compiled in Table II. The effect of the average specimen on the neutron flux in the stony mockup was only about 3%, and that in the iron mockup was 17%. The stony mockup was made to approximate the composition of the meteorite Allegan reported by MERRILL AND STOKES[16].

In the actual neutron activation of meteorites, the rare earth standards that were irradiated simultaneously with the meteoritic specimens were in 1.00 ml of an aqueous medium. Since the experiment described above showed that there was no significant difference in the activity induced in the thin rare earth sources inside the 5-g chondritic mockups and outside the mockups (see Table II), it was necessary to determine whether any difference in absorption and scattering effects occurred between the thin rare earth sources and the rare earths in 1.00 ml of aqueous medium. An average ratio of 1.00 ± 0.05 for the fourteen rare earths was determined as the activity ratio between thin-rare earth sources and a rare earth in 1.00 ml of solution, both of which were irradiated simultaneously. Therefore, it was concluded that the neutron intensities and spectra throughout the 5-g chondritic or achondritic specimens are identical within ±8% to those of the rare earth standards in 1.00 ml of aqueous medium.

TABLE II

RATIO OF NEUTRON FLUXES INSIDE AND OUTSIDE OF CHONDRITIC AND IRON MOCKUPS AS MEASURED BY RARE EARTH STANDARDS[a]

| *Rare earth*[b] | *Ratio of activity outside to activity inside of mockups* | | *Rare earth*[b] | *Ratio of activity outside to activity inside of mockups* | |
|---|---|---|---|---|---|
| | *Chondritic mockup* | *Iron mockup* | | *Chondritic mockup* | *Iron mockup* |
| ${}^{140}_{57}La$ | 1.02 | 1.19 | ${}^{160}_{65}Tb$ | 1.03 | 1.13 |
| ${}^{141}_{58}Ce$ | 1.04 | 1.23 | ${}^{165}_{66}Dy$ | 1.05 | ≈1.21 |
| ${}^{143}Ce$ | 1.03 | ≈1.20 | ${}^{166}_{67}Ho$ | 1.02 | 1.21 |
| ${}^{142}_{59}Pr$ | 0.97 | 1.16 | ${}^{171}_{68}Er$ | 1.01 | 1.21 |
| ${}^{147}_{60}Nd$ | 1.04 | — | ${}^{170}_{69}Tm$ | 1.05 | <1.11 |
| ${}^{141}_{61}Pm$ | 1.04 | — | | | |
| ${}^{151}_{61}Pm$ | 1.01 | ≈1.15 | ${}^{175}_{70}Yb$ | 1.04 | ≈1.11 |
| ${}^{153}_{62}Sm$ | 1.00 | 1.15 | ${}^{177}_{70}Yb$ | 1.00 | — |
| ${}^{152m}_{63}Eu$ | 1.02 | ≈1.23 | ${}^{176}_{71}Lu$ | 1.01 | ≈1.10 |
| ${}^{152}_{63}Eu$ | — | 1.23 | ${}^{177}_{71}Lu$ | 0.98 | 1.17 |
| ${}^{159}_{64}Gd$ | 1.03 | ≈1.12 | | | |

[a] The chondritic mockup was a 10-g sample with a thin rare earth oxide source in the center. The iron mockup was a 12-g pure iron bar (1.27 cm in diameter and 1.27 cm long) with a thin rare earth oxide source in the center.

[b] See Table I for the neutron-capture reactions.

Since the average rat irradiated inside the iron bar to that of the sourc .17 ± 0.05, the average effect throughout an iron spe it is concluded that the neutron intensities and spectra o imens are 1.09 ± 0.08 times less than the corresponding n spectra of the rare-earth standards in 1.00 ml aqueous medi

Usually the meteoritic not machined to the dimensions of the iron bars that were used ximate measurement of the reduction in neutron intensities. Appl e correction factor of 1.09 to all of the rare earth abundances in iron will not significantly alter the ratio of absolute abundances of the rare e ondrites to those in irons of ∼$10^4$, found recently by VASILEVSKIS *et al.*[17]. At n error of *ca.* 5% would be introduced in the relative rare earth abundances if th actor of 1.09 were applied to all rare earth abundances in 10-g specimens of iron meteorites.

It is evident from the discussion above that both relative and absolute abundances of all rare earths may be precisely determined by neutron-activation analysis only if all the rare earths are distributed homogeneously throughout the entire meteoritic specimen. Since many of the rare earth elements have high thermal and epithermal neutron-absorption cross sections, they may be responsible for self-shadowing effects. In such a case, only the relative rare earth abundances may be ascertained, since the rare earth elements may be concentrated (homogeneously with respect to themselves) in minuscule crystals or grains throughout the meteorite. Furthermore, if the rare earth elements are individually concentrated in separate minuscule crystals and grains throughout the matrix, the absolute abundances may be determined only for elements that have relatively low neutron-absorption cross sections (200 barns or less).

A consideration of ion-radii shows that occurrence of individual rare earth separation is highly unlikely. However, it is possible that the light and heavy rare earth groups may be fractionally separated and may thereby introduce errors in both the absolute and relative abundance values.

A few simple calculations illustrate the seriousness of self-shadowing. Let us assume that all the lanthanum in a meteorite is concentrated in a sphere in the form of the oxide, and that the quantity of lanthanum is equal to that found in the chondrites Allegan or Richardton[14], namely, $1.6 \cdot 10^{-6}$ g of lanthanum per 5 g of meteorite. Since lanthanum has a thermal-neutron absorption cross section of 8.9 barns, the neutron flux at the center of the $La_2O_3$ sphere would be slightly depressed by about 0.1%. On the other hand, let us assume that a quantity of europium equal to $0.4 \cdot 10^{-6}$ g of europium per 5 g[14] of meteorite is concentrated in a sphere in the form of $Eu_2O_3$. The europium neutron-absorption cross section of 4300 barns would cause a severe neutron-flux depression of approximately 22%. If lanthanum and europium were homogeneously mixed and concentrated in a single sphere, the neutron flux would again be depressed by about 20%, which would make the determination of the absolute abundance of either lanthanum or europium impossible. However, the relative abundance ratio of lanthanum to europium could be precisely determined, since the neutron flux in each infinitesimal volume element in the sphere would be the same for both lanthanum and europium.

In order to determine the extent of the rare earth self-shadowing effect, it is necessary to determine and to compare the abundances of the rare earths in meteorites by using different analytical methods. The most obvious method is the standard spectrographic technique. One of its principal disadvantages is the possible introduction of rare earths during chemical manipulation. By far the best method is to determine the rare earth elemental abundances by photoneutron-activation analysis. This method differs from the standard neutron-activation analysis in that the activated rare earth radioisotopes are induced by $(\gamma,n)$ reactions. The necessary $\gamma$-ray fluxes are generated by a high-intensity, 20- to 50-MeV electron linear accelerator. The rare earths Ce, Nd, Sm, Eu, Gd, Er, Tm, Yb and Lu are amenable to the photoneutron analysis with no accompanying self-shadowing effect.

Approximately 250 mg of zirconium is dissolved from the crucible during the fusion. Since the rare-earth mineral xenotime is accompanied by the mineral zircon, from which the zirconium crucible was probably derived, an activation analysis was carried out on a part of a zirconium crucible lid. No rare earth $\gamma$-lines were observed. Upper limits were calculated for the individual rare earth abundances that diluted the added carriers. The maximum carrier dilution was calculated to be less than 2%, and the average less than 1%.

A typical elution spectrum for rare earths and scandium removed from a cation ion-exchange column is given in Fig. 1. This spectrum applies to the rare earths activated in the chondritic meteorite Allegan. $\gamma$-ray intensities vary from a few hundred to several hundred thousand counts per min. It is apparent that a single elution through an ion-exchange column is satisfactory. However, in this case the long-lived $^{46}$Sc (85 days) contributed appreciably to the lutetium, ytterbium, and thulium peaks; this can be avoided by removing most of the scandium from the rare earths before separating them in the ion-exchange column. This modification of the technique has been included in the procedure outlined above in *Further procedure for both stony and iron meteorites*.

Thulium, represented by 129-day $^{170}$Tm, is on the trailing edge of the peak for the eluted element ytterbium. Consequently, some 32-day $^{169}$Yb may interfere with the assaying of the thulium abundance if time is not allowed for the $^{169}$Yb to decay. To separate thulium from ytterbium, a second elution of the collected thulium peak activity may be performed by passing thulium through a freshly prepared and uncontaminated ion-exchange column at a pH of 3.2.

From Fig. 1, it also appears that gadolinium, separated on the leading edge of the high europium peak, should be subjected to a second elution for better resolution. However, one ion-exchange pass is adequate for gadolinium, because (*1*) any 9.2-h $^{152m}$Eu atoms present in the separated 18-h $^{159}$Gd decay at approximately twice the rate of the $^{159}$Gd; (*2*) the leading edge of the europium peak is sufficiently steep that only a small percentage of the europium fraction will be found in the gadolinium fraction; and (*3*) the high-energy $\gamma$-rays of 9.3-h $^{152m}$Eu are discriminated against by selectively counting (window counting) the low-energy $\gamma$-rays of 18-h $^{159}$Gd. In other meteorite analyses for rare earths, the gadolinium and europium peaks were clearly resolved.

In some cases, it is desirable to measure only the relative abundance ratio of the light and heavy rare earth groups and to eliminate employment of the ion-exchange technique to analyze the abundances of the entire rare earth group. For example, in meteorites, sediments, and rocks, the fractionation of rare earths into different phases may be measured. Two rare earths, lanthanum, via $^{139}$La (n,$\gamma$) 40-h $^{140}$La, and dysprosium, via $^{164}$Dy (n,$\gamma$) 2.32-h $^{165}$Dy, are particularly representative of the light and heavy groups, respectively. Furthermore, when the $\gamma$-rays and half lives of all the neutron-activated rare earths are considered, the characteristic high-energy $\gamma$-ray (1.60 MeV) of 40-h $^{140}$La and the short half life of 2.32-h $^{165}$Dy make the determination of the abundances of these two elements in a mixture of all the neutron-activated rare earths particularly suitable. The only assumed condition is that the relative abundances of all the rare earths do not markedly differ (perhaps by a factor of ten) from the abundances given for the two chondritic meteorites in Table I.

In addition to the rare earth elements and scandium, the abundance of the element yttrium may be determined by neutron-activation analysis. The general chemical and ion-exchange operations used for the separation of the rare earths are applicable to the separation of yttrium. Elution of yttrium from the ion-exchange column is at, or near, the elution of dysprosium. The $\beta$-radioactivity of 64-h $^{90}$Y and an yttrium standard are counted and compared to determine the abundance of the yttrium.

## ACKNOWLEDGEMENTS

We wish to thank Professor HANS E. SUESS of the University of California, La Jolla, for proposing to us the problem of determining the abundances of rare earths in meteorites through neutron-activation analysis. We are indebted to Professor JOHN W. IRVINE, JR., of the Massachusetts Institute of Technology for valuable suggestions. We also thank J. E. LASCH for help in the radioactivity measurements and D. A. OLEHY for his assistance in running the ion-exchange column.

## SUMMARY

The abundances of the rare earths, lanthanum through lutetium, have been determined in chondritic, achondritic, and iron meteorites by neutron-activation analysis. The procedure used should also be applicable to the analysis of terrestrial stones and sediments. After exposure to a thermal-neutron flux of $2 \cdot 10^{12}$ neutrons/cm$^2$/sec for 2 h, the chondritic or achondritic sample, with added rare earth carriers, is dissolved after sodium peroxide fusion. Iron specimens are dissolved in a hydrochloric acid medium. The rare earths are then separated as a group from the matrix and are individually separated by means of a Dowex 50 W-X12 cation resin column and elution with 1 *M* ammonium lactate. This method is sensitive to fractional parts per million of the individual rare earths. The abundance of scandium may also be determined in the same procedure.

## RÉSUMÉ

Un procédé a été mis au point pour le dosage des éléments des terres rares dans divers météorites et roches, en utilisant la méthode par activation au moyen de neutrons. Les terres rares sont isolées en un groupe, puis séparées individuellement au moyen d'une résine Dowex et élution par le lactate d'ammonium. Le scandium peut être déterminé par le même procédé.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung der seltenen Erden in Meteoriten und Gesteinen durch Aktivierung mit Neutronen. Die seltenen Erden werden als Gruppe abgeschieden und anschliessend mit einem Austauscherharz getrennt. Scandium kann nach der gleichen Methode bestimmt werden.

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*Anal. Chim. Acta*, 25 (1961) 10–24

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# EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

## I. DETERMINATION OF COBALT

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(Received December 9th, 1960)

### INTRODUCTION

The triphenylmethylarsonium cation has been applied to permanganate[1], dichromate[2] and iodine[3] titrations, using extractive end-points. This paper describes its application to the determination of cobalt by the addition of an excess but known amount of EDTA, and back-titration with a standard cobalt solution. At the end-point, the blue ion-association pair triphenylmethylarsonium tetrathiocyanato cobaltate(II) is extracted into chloroform.

A number of methods have been proposed for the estimation of cobalt with EDTA, including back-titration with other metals using Eriochrome Black T indicator[4–6] and direct titration using murexide indicator[7]. Thiocyanate has been used as an indicator in various aqueous solvent mixtures[7,8]. For example, cobalt has been determined in a $1:1$ acetone–water mixture by addition of an excess of EDTA, and back-titration with standard cobalt(II) solution; the method has been applied to the determination of a number of other metals[9–11].

Although the extractive method of end-point detection introduces an additional step in an analysis, this disadvantage is outweighed by several advantages, the two most important being: (*1*) the end-point is in no way affected by the presence of unreactive coloured ions or highly coloured metal–EDTA complexes; (*2*) the sensitivity of the end-point is increased by the use of a relatively small volume of extracting solvent.

## APPARATUS AND REAGENTS

Titrations were performed in a glass-stoppered 500-ml conical flask fitted near the base with a horizontal closed side-arm approximately 3 cm long and 2 cm in diameter. The appearance of the blue colour at the end-point is more easily seen when the chloroform is run into this closed side-arm.

### *Solutions used*

A.R. quality reagents were used wherever possible. Standard EDTA solution, 0.01 *M* solution of the disodium salt. This solution was standardised against zinc solution using Eriochrome Black T as indicator. Standard cobalt(II) solution, 0.01 *M* solution of iron-free cobalt ammonium sulphate. Buffer solution of pH 9.3 was prepared from 150 ml of concentrated aqueous ammonia (sp.gr. = 0.880) and 160 g of ammonium chloride, diluted to 1 l with water.

Solutions were prepared using distilled water which had been passed through a column containing cation exchange resin in the sodium form. Polythene containers were used for storage.

TABLE I

| *mg of Co added* | *mg of Co found* | *% Deviation from Co added* | *Mean mg of Co found* | *% Deviation of mean from Co added* | *Maximum % deviation of Co found from mean* |
|---|---|---|---|---|---|
| 1.214 | 1.244 | +2.5 | 1.228 | +1.2 | 1.6 |
| 1.214 | 1.208 | −0.5 | | | |
| 1.214 | 1.220 | +0.5 | | | |
| 1.214 | 1.238 | +2.0 | | | |
| 1.214 | 1.232 | +1.5 | | | |
| 3.035 | 3.047 | +0.4 | 3.034 | −(<0.1) | 0.4 |
| 3.035 | 3.029 | −0.2 | | | |
| 3.035 | 3.029 | −0.2 | | | |
| 3.035 | 3.023 | −0.4 | | | |
| 3.035 | 3.041 | +0.2 | | | |
| 6.070 | 6.137 | +1.1 | 6.098 | +0.5 | 0.6 |
| 6.070 | 6.082 | +0.2 | | | |
| 6.070 | 6.088 | +0.3 | | | |
| 6.070 | 6.100 | +0.5 | | | |
| 6.070 | 6.082 | +0.2 | | | |

## PROCEDURE

The sample cobalt solution (containing from 2 to 12 mg of cobalt* and 25 ml of standard EDTA solution are pipetted into the titration flask. If necessary, approximately 1 *M* ammonia is added until litmus paper just turns blue. Approximately 10 ml of chloroform are then added, followed by 2 ml of buffer solution, 5 ml of 50% potassium thiocyanate solution and 3 ml of 1% triphenylmethylarsonium chloride solution. The excess EDTA is then back-titrated with the standard cobalt solution.

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* For the estimation of more than 12 mg of cobalt, more EDTA solution should be added, or the concentrations of both EDTA and the cobalt solution used as back-titrant should be increased. The sample volume should not be more than 150 ml for the quantities of buffer, potassium thiocyanate and triphenylmethylarsonium chloride specified. For larger sample volumes, more of these reagents should be used.

The cobalt solution should be added dropwise as the end-point is approached, the flask being stoppered and shaken after the addition of each drop. The end-point is indicated by the appearance of a blue colour in the chloroform layer.

## RESULTS

The cobalt content of three different volumes of a solution of known concentration was determined by the suggested procedure. Results are shown in Table I.

With the exception of the first group of results, which were obtained by determining a smaller quantity of cobalt than that recommended in the procedure, it can be seen that the mean cobalt determined may be expected to be within 0.5% of the true value, while the maximum variation about this mean is also of the same order, thus leading to a maximum expected error of about 1% for any single determination. In the case of the samples with 1.214 mg of cobalt, the corresponding figures are approximately doubled; this is due not only to the comparatively large error in pipetting a small volume of solution (2 ml), but also to the large percentage errors inherent in calculations based on a small titration difference (*i.e.* the difference between the back-titration of excess EDTA and the titration of 25 ml of EDTA solution alone).

## DISCUSSION

Preliminary work indicated that sharp end-points could be obtained over the pH range 5–10. In order to stabilise the cobalt–EDTA complex as much as possible, the titration should be done at a high pH. An ammoniacal buffer of pH 9.3 was chosen, since it has maximum buffering capacity, and titrations performed in alkaline solutions up to pH 10 were highly reproducible.

The effect on the titration of varying the volumes of potassium thiocyanate, triphenylmethylarsonium chloride and buffer solutions was investigated. The titration results did not vary by more than 0.1 ml from that obtained using the specified reagent amounts, when the volumes of the reagents were varied within the limits: potassium thiocyanate, 1 to 30 ml; triphenylmethylarsonium chloride, 1 to 30 ml; and buffer, 0.5 to 8 ml (the volume of the aqueous solution at the end-point was in each case between 70 and 100 ml). However, the end-points observed when using the limiting amounts were in general less sharp than those obtained with the recommended quantities. When large volumes of the triphenylmethylarsonium chloride solution were used, lengthy shaking was required to avoid premature end-points.

The greater part of the work described in this paper was performed with $M/100$ solutions of EDTA and cobalt, and sharp end-points were obtained. However, titrations carried out using $M/1000$ solutions gave somewhat diffuse end-points. In contrast, titrations using $M/10$ solutions gave very sharp end-points, provided that more buffer was used. Consequently, solutions of this concentration could be used in the determination of comparatively large amounts of cobalt without interference from the colour of the red cobalt–EDTA complex.

The blank was found to be approximately 0.02 ml when using $M/100$ solutions, and was therefore neglected.

The solution of cobalt and excess EDTA should, if necessary, be first neutralised with ammonia. The order of addition of the chloroform and the other reagents was found to have no effect on the result.

The effect of using other quaternary arsonium cations in the extractive end-point titration was investigated. For this purpose, 3 ml of a 1% aqueous solution of the arsonium salt under test was used. The $Me_4As^+$ and $PhMe_3As^+$ cations failed to form chloroform-soluble ion association pairs with the $[Co(SCN)_4]^{-2}$ anion. In contrast, the $Ph_2Me_2As^+$ and $Ph_4As^+$ ions gave titration results identical with those obtained when using the $Ph_3MeAs^+$ ion.

## SUMMARY

A method for the determination of cobalt by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending upon the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the estimation of cobalt in highly coloured aqueous solutions. Average errors can be expected to be less than 0.5%.

## RÉSUMÉ

Une méthode est proposée pour le dosage du cobalt, par addition d'EDTA en excès et titrage en retour au moyen d'une solution étalon de cobalt. Le point final est décelé par extraction du composé bleu $[Ph_3MeAs]_2[Co(SCN)_4]$ dans le chloroforme ($Ph_3MeAs$ = triphénylméthylarsonium).

## ZUSAMMENFASSUNG

Beschreibung einer indirekten komplexometrischen Methode zur Bestimmung von Kobalt mit EDTA in Gegenwart von Triphenylmethylarsoniumchlorid, Rhodankalium und Chloroform. Der Endpunkt wird durch das Auftreten einer blauen Färbung in der Chloroformschicht angezeigt.

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# A SOLVENT EXTRACTION METHOD FOR THE SEPARATION OF IODIDE

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(Received December 21st, 1960)

The present study was undertaken as a means of establishing the possible usefulness of solvent extraction methods in the separation of anions. Although the separation of anions[1-3] has always remained a difficult problem, and although solvent extraction methods have become increasingly popular in the separation of cations, the possibility of combining the two fields has remained essentially unexplored. The separation of iodide, as reported here, is only one of a number of promising anion separations now under investigation.

Following the classification proposed by MORRISON AND FREISER[4], it can be seen that anion extraction systems might be envisaged, based on the extraction of either an ordinary coordination compound,

$$M^{+n} + nX^{-} = MX_{n}$$

or an ion-association complex,

$$M^{+n} + (n + a)X^{-} = MX^{-a}_{(n+a)}$$

$$MX^{-a}_{(n+a)} + aY^{+} = [aY^{+}, MX^{-a}_{(n+a)}] \qquad [\text{ion-association complex}]$$

Because the halides form stable complexes with a number of metal ions, it was decided to investigate them first. High concentrations of iodide have been used for the solvent extraction of metal ions such as mercury(II), cadmium, antimony(III), gold(III), indium(III), lead(II), thallium(III), and tin(II). Iodides of bismuth(III), iron(II), copper(II) and palladium(II) are also extractable, albeit to a lesser degree[5]. Preliminary qualitative work showed the iodide ion to extract very well with either cadmium or mercury(II) as the coordinating cation using a 1 : 1 solvent mixture of tributyl phosphate (TBP) and methyl isobutyl ketone (MiBK). WEST AND TRON[6] studied the extraction of the halides of mercury(II) and found that optimum extraction (about 97%) was obtained only at a Hg : halide ratio of 1 : 2; at a ratio of 2 : 1, the amount of halide extracted decreased to about 82%. On the other hand, excess cadmium had very little effect on the efficiency of extraction of iodide. Because in actual analysis the amount of a constituent is seldom known beforehand, it is generally impossible to anticipate the optimum amount of a critical reagent to be added; therefore, a procedure that can tolerate a reasonable excess of reagent is to be preferred. The cadmium iodide system using 1 : 1 TBP–MiBK as extractant seemed to possess many favorable characteristics and thus to warrant detailed study.

## EXPERIMENTAL

### *Reagents*

Reagents required for the isolation of iodide include: (*1*) Cadmium nitrate (1 *N*); (*2*) Carbon tetrachloride; (*3*) Sulfuric acid (6 *N*); (*4*) Sodium hydroxide (1 *N*); (*5*) Methyl isobutyl ketone; (*6*) Tri-*n*-butyl phosphate.

All chemicals used in these studies were A.R. grade.

### *Choice of solvents*

WEST AND TRON[6] found that a mixture of tributyl phosphate and ethyl acetate gave essentially complete extraction of the halides of mercury in a single pass. On the other hand, MORRISON AND FREISER[4] recommend methyl isobutyl ketone for the extraction of various cations using iodide as the complexing additive. After considering these and other solvents, a 1 : 1 TBP–MiBK mixture was selected because of its extractive efficiency and because it was found to be relatively insensitive to changes in acidity.

### *Recovery of iodide*

For the recovery of extracted iodide, the usual technics used in extraction methods were tried and found ineffective. Finally, a new approach[7] was introduced, that of adding a third solvent, miscible with the non-aqueous solvents but very poor at extracting iodide. The addition of carbon tetrachloride, about twice as much as the volume of the TBP–MiBK layer, produced dramatic results. A yellow color developed after a minute or two of standing. At this point, addition of 1 *N* sodium hydroxide (20 ml) gave a two-phase system composed of an upper aqueous layer and a lower non-aqueous layer. The large proportion of carbon tetrachloride made the non-aqueous layer the heavier one. After a minute of vigorous shaking, a white precipitate of cadmium hydroxide formed in the aqueous phase, and the yellow color disappeared from the TBP–MiBK–$CCl_4$ layer. The recovery of the iodide from the non-aqueous phase using the solvent displacement technic just outlined proved to be remarkably efficient. It is of interest to note that this is a reverse of the established practice of using solvent mixtures to effect increases in solvent extraction efficiencies.

### *Experimental procedures*

10 ml of cadmium iodide solution were pipetted into a 60-ml separatory funnel. Dilute sulfuric acid was then added to bring the solution to the desired pH. To this acidified solution, an equal volume of a 1 : 1 mixture of TBP and MiBK was added, and the mixture shaken for about 30 sec to insure contact between the two immiscible liquids. The separatory funnel containing the mixture was immersed in a thermostat kept at 30°, where the system was allowed to come to equilibrium.

After equilibration, the non-aqueous layer was treated with 20 ml of carbon tetrachloride and the mixture then shaken with 20 ml of 1 *N* sodium hydroxide to recover the cadmium and iodide. Copious precipitation of white cadmium hydroxide resulted, and the iodine was released in the form of $I^-$, possibly including small amounts of $OI^-$.

The $CCl_4$–TBP–MiBK layer was washed twice with 20-ml portions of 1 *N* sodium hydroxide, and the washings were combined with the first one containing the cadmium hydroxide precipitate. This mixture was made 6 *N* in regard to hydrochloric acid, and the iodine determined using a conventional iodine monochloride procedure.

Cadmium was determined in the aqueous layer using a dithizone extraction procedure on suitable aliquots of the solution. The cadmium in the non-aqueous layer and the unextracted iodide were obtained by difference.

Cadmium iodide solutions used for the initial concentration studies were standardized using hot alkaline permanganate oxidation of the iodide followed by thiosulfate titration. A small amount of silver nitrate solution was added halfway in the titration to sharpen the end-point[8].

To acquire a better understanding of the extraction of cadmium iodide, and in particular, the iodide, the effects of various factors were studied. These factors were the hydrogen ion concentration, the cadmium to iodide molar ratio, the initial concentration of the cadmium iodide solution, and the effect of temperature.

### *The hydrogen ion concentration*

As shown in Table I, the system is not very sensitive to changes in hydrogen ion concentration. A twenty-fold change in pH occasioned only a 2% decrease in the iodide extracted.

TABLE I

| | *pH* | | | | | |
|---|---|---|---|---|---|---|
| | *0.3* | *0.6* | *1.0* | *2.0* | *3.0* | *6.0* |
| Percentage I extracted | 96 | 95 | 95 | 94 | 94 | 94 |
| Percentage Cd extracted | 68 | 70 | 82 | 93 | 95 | 96 |
| Cd: I mole ratio in extract | 1/2.8 | 1/2.7 | 1/2.4 | 1/2 | 1/2 | 1/2 |
| Δ pH in aqueous phase | +0.2 | +0.1 | +0.1 | +0.5 | +0.3 | −3.2 |

For pH values less than 0.3, there is extensive atmospheric oxidation of the iodide. On the other hand, starting at pH 2, a whitish emulsion forms in the non-aqueous layer which takes longer to clear up as the pH increases further.

Unless otherwise stated, the cadmium iodide solutions used were approximately 0.05 *M* in concentration.

### *The cadmium to iodine molar ratio*

If any metal ion is to be of practical use in the separation of anions by solvent extraction, its presence in excess should not appreciably decrease the extraction efficiency. Fortunately, the cadmium ion proved to be very satisfactory for iodide extractions when considered on this basis.

TABLE II

CADMIUM TO IODIDE RATIO IN AQUEOUS LAYER

| | *1:2* | *1:1* | *2:1* | *4:1* |
|---|---|---|---|---|
| Percentage I extracted | 95 | 95 | 92 | 89 |
| Percentage Cd extracted | 70 | 50 | 24 | 20 |
| Cd : I mole ratio in extract | 1/2.7 | 1/1.8 | 1/1.9 | 1/1.3 |

The above data were obtained at 30° and at pH 0.6 of the aqueous layer.

### *The initial concentration of the cadmium iodide solution*

Data show that starting with solution strengths approximating those usually encountered in analysis (0.05–0.1 *M*), almost complete separation of the iodide ion using $Cd^{+2}$ as the coordinating cation can be attained in two or three extractions.

TABLE III

INITIAL CONCENTRATION OF THE $CdI_2$ SOLUTION

| | *0.001 M* | *0.003 M* | *0.006 M* | *0.01 M* | *0.03 M* | *0.05 M* | *0.1 M* |
|---|---|---|---|---|---|---|---|
| Percentage I extracted | 61 | 77 | 87 | 91 | 95 | 95 | 96 |
| Percentage Cd extracted | 60 | 53 | 66 | 69 | 70 | 70 | 75 |
| Cd : I mole ratio in extract | 1/2 | 1/3.7 | 1/2.6 | 1/2.7 | 1/2.7 | 1/2.7 | 1/2.6 |

Temperature = 30°, pH = 0.6

### *Effect of temperature*

Because the solvent mixture is inflammable, the study of temperature effects was not extended beyond 40°. Moreover, the system seems to behave in accordance with BJERRUM's theory. For solvents of low dielectric constant, theory predicts a decrease in ion association with increase in temperature. Since the extracting species are presumably ion association complexes, the decrease in extraction as the temperature was raised to 40° is in agreement with theory.

TABLE IV

| | *Temperature* | | |
|---|---|---|---|
| | *25°* | *30°* | *40°* |
| Percentage I extracted | 97 | 95 | 94 |
| Percentage Cd extracted | 68 | 70 | 68 |
| Cd : I mole ratio in extract | 1/2.9 | 1/2.7 | 1/2.8 |

### *Selectivity*

A qualitative survey of the common anions was conducted to find out which of them would be extracted under the same conditions. Varying degrees of extractability were encountered and may be classified according to the following groups:

(*1*) Anions that were extracted with approximately the same efficiency as the iodide: $CN^-$ and $CNS^-$.

(*2*) Anions extracted to a moderate degree: $Cl^-$, $Br^-$, $C_2O_4^{-2}$, and $NO_3^-$.

(*3*) Anions that were extracted very poorly or not at all: $F^-$, $S_2O_3^{-2}$, $SO_4^{-2}$, $PO_4^{-2}$, $Ac^-$, $S^{-2}$, $Fe(CN)_6^{-4}$, and $BO_3^{-3}$.

No evidence of coextraction was found.

## DISCUSSION

Cadmium iodide solutions are known to contain the following ionic and molecular species: $Cd^{+2}$, $CdI^+$, $CdI_2$, $CdI_3^-$, $CdI_4^{-2}$ and $I^-$. The simple cadmium and iodide ions are probably found only in negligible amounts, since cadmium iodide is a weak electrolyte, except in very dilute solutions[9]. Working with neutral solutions of ionic strength 3, LEDEN[10] found the iodide complexes of cadmium present in the following decreasing order of abundance: $CdI_4^{-2}$, $CdI_3^-$, $CdI_2$ and $CdI^+$. ALBERTY AND KING[11], on the other hand, obtained from mobility data, using solutions of ionic strength of 0.5 and a total iodide concentration of 0.1 *M*, the following values for the cadmium iodide complexes:

$Cd^{+2}$ ------ negligible
$CdI^{+}$ ------ 6%
$CdI_2$ ------ 12%
$CdI_3^{-}$ ------ 16%
$CdI_4^{-2}$ ------ 62%

Their graphs of fraction of complex *vs.* total iodide concentration where the above values were read off showed that the relative amounts of the different complexes varied with the total iodide concentration. HARRIS[12] reported from ion exchange experiments, using 0.0666 *M* $CdI_2$, the presence of $CdI_4^{-2}$, $CdI_2$ $CdI_3^{-}$ and $CdI^{+}$, in that order of increasing abundance.

In the present studies, the solutions were acidic. Undoubtedly, all the different complexes of cadmium with iodide would still be present. The question is which forms predominate over the others? For simplicity, the formulas of the cadmium iodide complex ions were written unhydrated, although it is known that molecules of water are coordinated to the central ion. $CdI_2$, for example, is really $Cd(H_2O)_4I_2$. With this in mind, it is possible that the addition of hydrogen ions, which have a great affinity for water molecules, makes it relatively easier for the coordinated water to leave the sphere of influence of the central metal ion and for the simple iodide ions to take over the vacated positions. In solutions of low pH, say 0.3 and 0.6, the principal cadmium iodide complexes are probably, in decreasing order of abundance, $CdI_3^{-}$, $CdI_2$ and $CdI_4^{-2}$. At higher pH values, the following are probably present to a greater extent: $CdI_2$ and $CdI^{+}$. The data in Table I point to the following as the uncharged species extracted from solutions of low pH: $[H^{+}, CdI_3^{-}]$, $CdI_2$ and $[2\ H^{+}, CdI_4^{-2}]$. The increased participation of the last named ion association complex should be expected with further increase in acidity. From pH 2 on up to higher pH values, the extracted species are probably $CdI_2$ and $[CdI^{+}, OH^{-}]$ with the latter making its greatest participation at pH 6, as evidenced by the increase in the acidity of the aqueous phase, an increase which is too great to attribute to a possible increase in the solubility of water in the TBP–MiBK phase.

The relative insensitivity to pH change may be due to the existing equilibria among the different complexes of cadmium and iodide which allow interconversion from one major ionic species to another that can form an uncharged extractable complex at the new pH.

As long as the higher ion association complexes are the major species being extracted, the extraction efficiency of iodide is high. Addition of cadmium ions to vary the Cd : I mole ratio increases the ionic strength of the solution, making extensive ion association possible. However, the concurrent chemical effect limits the ion association to the lower complexes as shown by the following equations:

$$Cd^{+2} + CdI_4^{-2} \rightarrow 2\ CdI_2$$
$$Cd^{+2} + CdI_3^{-} \rightarrow CdI_2 + CdI^{+}$$
$$Cd^{+2} + CdI_2 \rightarrow 2\ CdI^{+}$$

The uncharged species being extracted are probably $CdI_2$, and $[CdI^{+}, NO_3^{-}]$ with the latter increasing in importance with increase in Cd : I ratio. The solution added to increase the cadmium to iodide ratio was cadmium nitrate which explains the appearance of the nitrate ion here. No attempt was made to estimate the amount of nitrate extracted, but its presence was detected.

The increase in extraction with increase in initial concentration of the cadmium iodide solution may be due to the ionic-strength and mass-action effects. The former favors ion-association complex formation which, because of the mass-action effect and the presence of hydrogen ions, would in turn favor the higher complexes, $CdI_3^-$ and $CdI_4^{-2}$:

$$2\,CdI_2 \rightarrow CdI_3^- + CdI^+$$
$$3\,CdI_2 \rightarrow CdI_4^{-2} + 2\,CdI^+$$

At lower concentrations, the amount of simple cadmium and iodide ions increases, but enough complexes are still present to sustain the formation of extractable species. The data in Table III point to $[2\,H^+, CdI_4^{-2}]$, $[H^+, CdI_3^-]$ and $CdI_2$ as the predominant forms being extracted with the participation of $[2\,H^+, CdI_4^{-2}]$ reaching its peak at 0.003 *M*. Apparently, the $CdI^+$ ion, which is the predominant species at very low $CdI_2$ concentrations, is unable to form an extractable uncharged ion association complex, the pH of the solutions (~pH 0.6) being so low as to make the formation of $[CdI^+, OH^-]$ highly improbable.

BJERRUM's theory predicts that an increase in temperature will cause a decrease in ion association in the TBP–MiBK phase. In the aqueous layer, the number of ion association complexes should increase. Of these two opposing effects, the data seem to indicate the predominance of the former.

## ACKNOWLEDGEMENT

The financial support of the Esso Standard Oil Company is gratefully acknowledged.

## SUMMARY

Solvent extraction is proposed for the isolation of anions. Data obtained in the extraction of iodide using cadmium as complexing agent under the influence of such factors as pH, addition of excess cadmium ions, initial concentration of the cadmium iodide solution and temperature are presented.

## RÉSUMÉ

L'extraction par solvant est proposée pour la séparation des anions. Les auteurs ont examiné l'influence de divers facteurs sur l'extraction de l'iodure au moyen de cadmium comme réactif complexant.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Anionen durch Lösungsmittelextraktion. Jodide werden als Cadmiumkomplexe mit einem Gemisch von Tributylphosphat–Methylisobutylketon abgetrennt. Der Einfluss verschiedener Faktoren auf die Extrahierbarkeit wurde untersucht.

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# TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE*

## II. THE SIMULTANEOUS DETERMINATION OF THE HALOGENS IN THE PRESENCE OF EACH OTHER

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(Received January 19th, 1961)

### INTRODUCTION

Most of the methods proposed for the simultaneous microdetermination of two or more halogens in organic compounds have been based either on lengthy gravimetric determinations[1,2], or have involved separations of the individual halogens. It would seem from the work of MAHR AND OTTERBEIN[3] that the completeness of such halogen separations is rather questionable on the micro scale.

Few titrimetric methods have been reported for the simultaneous determination of halide mixtures. The method of BERG[4] has been reported as unreliable[3]. VOROB'EV[5] has modified this method, but his optimum concentrations for each halogen are not suitable for application on the micro scale. A method has been proposed[6] for the micro determination of the three halogens in the presence of fluorine, and this was considered the most promising for adaptation to the rapid combustion procedure.

The titrimetric procedures recommended previously for the individual halogens were based on this work, but it was still necessary to establish satisfactory absorption conditions for the simultaneous determination of any combination by the rapid combustion method. Moreover, because the method required the use of aliquots for the determination of the individual halogens, the accuracy of the titrations involved had to be studied to ensure that it did not fall below the generally accepted limits.

### DISCUSSION

#### *The absorption of halogen combustion products*

Earlier work[7] has shown that the principal products of the rapid combustion are carbon dioxide, water vapour, the free halogens and, depending on the original elemental composition of the compound, variable amounts of nitrogen, nitrogen oxides and sulphur oxides together with some nitric and sulphuric acids. Some hydrogen chloride is formed during the combustion of certain types of chloro compounds, notably those which also contain sulphur. In the selection of suitable absorbents for these gaseous mixtures, any possible side-reactions between the halogens or their absorption products must be considered because of possible interference in the later titrations. For example, halate formation would vitiate a direct halide determination; to prevent this, an efficient reductant must be present in the absorbent.

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### *Hydrogen peroxide as a reductant*

Hydrogen peroxide has some advantages as a reductant for the absorption of the combustion products of organic chloro and bromo compounds because the determination can be completed acidimetrically when nitrogen and sulphur are absent[7]; the possibility of a total acidity determination on chloro-bromo materials of this type was considered, but the absorption behaviour of such compounds proved to be variable.

When neutral hydrogen peroxide solution was used as absorbent, chlorine was quantitatively absorbed but bromine gave results which were about 1% low. Hydrogen peroxide was generally satisfactory under alkaline conditions, but in one case there was evidence that some bromate formation had occurred. In this exceptional case mixtures of *p*-bromobenzoic acid and hexachlorobenzene were used and the amounts of elemental chlorine formed were substantially greater than those from most single chloro-bromo compounds. Presumably, either the chlorine reacted preferentially with bromide instead of peroxide, or, under the alkaline conditions some transiently formed hypochlorite reacted with elemental bromine. Either reaction would lead to bromate formation.

Not unexpectedly, similar evidence was obtained of iodate formation (to the extent of 30–50%) when the combustion products from chloro-iodo compounds were absorbed in alkaline peroxide. When, however, these halogenated compounds also contained sulphur, it was found that absorption was quite satisfactory in alkaline peroxide. It would seem that the sulphur dioxide formed during such combustions preferentially reduces all traces of hypohalite ions, before the hydrogen peroxide can assume its dual role as an oxidising and reducing agent in this absorption. Except for this particular application, the use of hydrogen peroxide cannot be recommended for the absorption of the mixed halogen products from the rapid combustion procedure.

### *Sulphur dioxide as a reductant*

Sulphur dioxide under alkaline conditions was found to be the best general reductant for the absorption of any of the halogen combinations. All excess had to be destroyed before the recommended titrimetric finishes were applied. High concentrations of electrolytes, such as sodium sulphate, formed during the neutralisation of the solutions interfered with the end-point in the chlorine determination; this difficulty was eliminated by keeping the alkali strength of the bisulphite absorption medium below 0.1 *N*.

### *Accuracy of the simultaneous evaluation procedures*

In general the percentages of the individual halogens in di- and trihalogenated organic compounds are lower than those in mono-halogenated substances. The percentage of chlorine in organic compounds containing one or both of the other halogens is usually small.

The use of aliquots also reduces the effective concentrations of the various halogens. This difficulty is largely compensated for the iodine and bromine micro determinations by use of the amplification methods of LEIPERT[8] and KOLTHOFF AND YUTZY[9] but there is no analogous amplification procedure available for chlorine.

For the evaluation of the total halogens, the mercuric oxycyanide method of VIEBÖCK[10] appeared to be the most convenient. The chloride can be determined subsequently by means of a comparison titration procedure[6,7] after deduction of the independently determined acid equivalents for the other halogens, but because the titration values for such chloride determinations are usually small, more care is needed during the titration; however, if sufficient sample (10–12 mg) is taken and if the titration is done from a 5-ml microburette (preferably graduated in 0.01-ml intervals) with a 0.005 $N$ titrant solution, reasonably satisfactory results (within ±0.30%) can be obtained for the chlorine.

The accuracy of the amplification procedures for bromine and iodine, was found to be well within the usual limits for microanalysis (±0.15%), despite the reduced concentrations in the aliquots. Accordingly, in view of the lower stability of 0.01 $N$ solutions of sodium thiosulphate, it was considered advisable to retain the usual 0.02 $N$ solution.

### *Simultaneous determination of chlorine and bromine*

With neutral hydrogen peroxide as absorbent, these two halogens were incompletely recovered from organic compounds containing oxygen or nitrogen. An alkaline bisulphite absorbent must, therefore, always be used for such compounds. On the other hand, alkaline peroxide absorbents cause no trouble when sulphur is also present in the compound, whether or not oxygen and nitrogen are present.

With either of these absorbents, chlorine and bromine are recovered as their halides in association with small concentrations of other electrolytes, notably sodium sulphate and nitrate. Two aliquots of the absorption solution are taken: the bromine is determined in one aliquot by the hypochlorite oxidation procedure[9], and the second aliquot neutralised and treated with mercuric oxycyanide to obtain the total halide content. The acid equivalent of the bromide is deducted and the chloride is then determined on the same aliquot by means of the comparison titration method mentioned earlier[6,7].

TABLE I

| *Compound* | *Sample weight in mg* | *% Bromine* | | *% Chlorine* | |
|---|---|---|---|---|---|
| | | *found* | *calculated* | *found* | *calculated* |
| *p*-bromobenzoyl chloride | 8.166 | 36.39 | 36.40 | 16.06 | 16.15 |
| | 7.017 | 36.29 | | 16.11 | |
| *p*-chlorobromobenzene | 6.987 | 41.72 | 41.74 | 18.63 | 18.53 |
| | 6.856 | 41.58 | | 18.57 | |
| 2-bromo-2′-chloroazobenzene | 7.867 | 26.92 | 27.04 | 11.90 | 12.00 |
| 2 : 6-dibromoquinone-4-chlorimide | 6.473 | 53.51 | 53.39 | 11.83 | 11.84 |
| 6-chloro-2 : 4-dibromoaniline | 6.870 | 56.09 | 56.01 | 12.39 | 12.42 |
| *p*-bromobenzene sulphonyl chloride | 6.979 | 31.20 | 31.27 | 13.97 | 13.87 |
| S-benzyl thiouronium chloride + | 3.786 | | | | |
| *p*-bromobenzoic acid | 5.838 | 39.70 | 39.75 | 17.41 | 17.49 |

Satisfactory values were obtained on a variety of organic materials; the results given in Table I show that both chlorine and bromine can be determined simultaneously with an accuracy of 0.10%.

*Simultaneous determination of chlorine and iodine*

Preliminary experiments showed that peroxide media are unsuitable for the simultaneous absorption of these two halogens. However, alkaline bisulphite solutions were quite satisfactory absorbents, whether or not nitrogen and/or sulphur were present. The titrimetric methods for these two halogens are analogous to those outlined above. Thus, the iodide in one aliquot is determined by the LEIPERT method[8] and chloride plus iodide is determined in a second aliquot by the mercuric oxycyanide method.

TABLE II

| *Compound* | *Sample weight in mg* | *% Chlorine* | | *% Iodine* | |
|---|---|---|---|---|---|
| | | *found* | *calculated* | *found* | *calculated* |
| *p*-chloroiodobenzene | 6.449 | 14.84 | 14.87 | 53.09 | 53.22 |
| | 7.185 | 14.82 | | 53.13 | |
| *p*-chlorobenzoic acid + *o*-iodobenzoic acid | 3.755 | | | | |
| | 3.989 | 22.42 | 22.65 | 51.22 | 51.17 |
| 5-chloro-7-iodo-8-hydroxyquinoline | 5.144 | 11.43 | 11.60 | 41.70 | 41.54 |
| *p*-chloroacetanilide + *o*-iodobenzoic acid | 3.079 | | | | |
| | 4.457 | 20.72 | 20.90 | 50.98 | 51.17 |
| *p*-chloroiodobenzene + benzyl disulphide | 6.886 | | | | |
| | 3.359 | 14.63 | 14.87 | 53.32 | 53.22 |
| 5-chloro-7-iodo-8-hydroxyquinoline + | 5.172 | | | | |
| benzyl disulphide | 3.164 | 11.52 | 11.60 | 41.43 | 41.54 |

The results on typical test compounds (Table II) show that chlorine and iodine can be determined by this method with an average absolute accuracy of ±0.14%. In view of the relatively small amounts of chlorine present in these compounds and the unfavourable conversion factor for the iodide acid equivalent, this accuracy must be considered satisfactory.

*Simultaneous determination of bromine and iodine*

Of the micro determinations available for bromine and iodine, those based on iodometric titration of the halates are undoubtedly the best. Attempts were made to exploit a controlled, two-stage iodometric titration of bromate and iodate based on studies by VAN DER MEULEN[11]; the method was satisfactory on pure halate solutions under the recommended acid-buffering conditions, but poor results were obtained when halides were oxidised to halates. The iodate recoveries were quite satisfactory but those for bromate were low. Detailed studies of this reaction have been postponed.

In the recommended method two aliquots are again required, iodine being determined in one by the LEIPERT procedure and the total iodine and bromine in the other by the hypochlorite oxidation procedure; the bromine is then calculated by difference[6].

Alkaline bisulphite solution was again found to be the most suitable absorbent for these two halogens in their various combinations with oxygen, nitrogen and sulphur.

The results, some of which are given in Table III, show that these halogens can be determined simultaneously with an accuracy of ±0.15%.

TABLE III

| *Compound* | *Sample weight in mg* | *% Bromine* | | *% Iodine* | |
|---|---|---|---|---|---|
| | | *found* | *calculated* | *found* | *calculated* |
| 2 : 4 : 6-tribromoiodobenzene | 7.376 | 54.41 | 54.40 | 28.81 | 28.79 |
| | 9.122 | 54.56 | | 28.88 | |
| *o*-bromoiodobenzene | 11.025 | 28.29 | 28.25 | 45.01 | 44.86 |
| 3 : 5-diiodo-2-hydroxybenzoic acid | 5.024 | | | | |
| + *m*-bromonitrobenzene | 4.550 | 39.42 | 39.56 | 64.96 | 65.09 |
| trimethyl ammonium iodide | 4.423 | | | | |
| + *p*-bromophenacyl bromide | 5.616 | 57.44 | 57.50 | 62.97 | 63.12 |
| 7-iodo-8-hydroxyquinoline-5-sulphonic acid | 8.554 | | | | |
| + *p*-bromophenacyl bromide | 4.579 | 57.31 | 57.50 | 36.13 | 36.14 |

TABLE IV

| *Compound* | *Cl* | *Br* | *I* |
|---|---|---|---|
| *1-iodo-2 : 4-dibromo-6-chlorobenzene* | | | |
| Halide present (mg) | 0.253 | 1.143 | 0.907 |
| Halide found (mg) | 0.248 | 1.139 | 0.905 |
| % theory | 8.95 | 40.33 | 32.02 |
| % found | 8.77 | 40.18 | 31.95 |
| *p-chloroiodobenzene + p-bromophenacyl bromide* | | | |
| Halide present (mg) | 0.312 | 1.268 | 1.118 |
| Halide found (mg) | 0.305 | 1.265 | 1.119 |
| % theory | 14.87 | 57.50 | 53.22 |
| % found | 14.53 | 57.33 | 53.26 |
| *o-iodobenzoic acid + p-bromobenzene sulphonyl chloride* | | | |
| Halide present (mg) | 0.285 | 0.643 | 1.376 |
| Halide found (mg) | 0.281 | 0.639 | 1.369 |
| % theory | 13.87 | 31.17 | 51.17 |
| % found | 13.71 | 31.10 | 51.00 |
| *6-chloro-2 : 4-dibromoaniline + 7-iodo-8-hydroxyquinoline-5-sulphonic acid* | | | |
| Halide present (mg) | 0.306 | 1.382 | 0.785 |
| Halide found (mg) | 0.314 | 1.385 | 0.786 |
| % theory | 12.42 | 56.01 | 36.14 |
| % found | 12.72 | 56.16 | 36.21 |

### *Simultaneous determination of chlorine, bromine and iodine*

The combustion products were absorbed in alkaline bisulphite solution. The absorption solution had to be divided into three aliquots for the subsequent finishes which involved determination of the iodide by the LEIPERT method, the total iodide and bromide by the hypochlorite oxidation procedure and the total halide by the method of VIEBÖCK[10]. The chlorine was then determined by the comparison titration method, after deducting the acid equivalents for iodine and bromine. Because all three titrimetric procedures used are unaffected by sulphate and/or nitrate ions, this method is of general applicability.

The three aliquot procedure reduces very considerably the effective halide concentrations in the solutions used for the final titration; but this difficulty can be offset by taking a larger sample weight of the order of 10–12 mg.

The results given in Table IV show that the accuracy for the determinations of bromine and iodine by this method is as good as that reported for their di-halogenated combinations (±0.15%). Not surprisingly, the values for chlorine were the least accurate (±0.30%) though in view of their dependence on the accuracy of the bromine and iodine values, this accuracy must be considered satisfactory.

## EXPERIMENTAL

### *A. The simultaneous determination of chlorine and bromine (in the absence of S)*

#### *Procedure*

The organic sample (4–8 mg) is burned as described previously[7] and the gaseous products are absorbed in 7–8 ml of 0.1 *N* sodium hydroxide containing 3–5 drops of 35% sodium bisulphite solution. The resulting absorption solution is transferred with the aqueous washings (4 × 3 ml) to a 100-ml lipped, conical flask and boiled for a few minutes with 2–3 drops of M.A.R. 30% hydrogen peroxide to destroy all excess of bisulphite. The solution is cooled, neutralised with 0.1 *N* sulphuric acid in presence of 3 drops of aqueous methyl red indicator solution and then made up to 50 ml in a graduated flask.

Two aliquots of 20 ml are taken for the two halogen determinations.

#### *Bromine determination*

The aliquot is placed in a 250-ml stoppered conical flask and analysed by the hypochlorite oxidation procedure (= *b* ml)[6,9].

#### *Total halide determination*

The second aliquot is transferred to a 100-ml conical flask and neutralised in presence of a definite amount of methyl red-methylene blue indicator solution (6–8 drops). After the solution has been treated with 10 ml of 2% mercuric oxycyanide solution (measured accurately), the alkali liberated is titrated with standardised 0.01 *N* sulphuric acid (= *a* ml).

#### *Chlorine evaluation*

In a matched 100-ml conical flask is placed an equal volume of neutral, distilled water and screened indicator solution, together with 10 ml of the mercuric oxycyanide solution and the amount of 0.01 *N* sulphuric acid which is calculated as equivalent to the chloride content ($a - b/3$). Finally, the comparison solution is titrated with 0.005 *N* sodium chloride solution until the colours in the two flasks are again matched.

#### *Blank determination*

It is essential to carry out a blank determination on all reagents, preferably using a sample of benzoic acid.

#### *Calculations*

Total halide titre: $a$ ml of 0.01 $N$ $H_2SO_4$

mg of $Br^-$ found in aliquot = $b$ ml of 0.02 $N$ $Na_2S_2O_3 \times 0.26639$

$Cl^-$ acid equivalent = $(a - b/3)$

mg of $Cl^-$ found in aliquot = $c$ ml of 0.005 $N$ $NaCl \times 0.1773$

### *B. Chlorine and bromine (in the presence of S)*

*Procedure*

The combustion is carried out as before but 7–8 ml of 0.1 *N* sodium hydroxide and 0.5 ml of 30% hydrogen peroxide are used as absorbent. The excess of peroxide is removed by boiling for several minutes in a 100-ml lipped conical flask. The solution is then cooled, neutralised with 0.1 *N* sulphuric acid in presence of aqueous methyl red solution and made up to 50 ml in a standard flask. The two halogen determinations are carried out exactly as described above with two separate aliquots of 20 ml.

### *C. The simultaneous determination of chlorine and iodine (in the presence or absence of N and/or S)* (a general method)

*Procedure*

The decomposition of the sample and treatment of the absorption solution are exactly as described under (*A*). Two aliquots of 20 ml are then taken.

*Determination of iodine*

A 20-ml aliquot is placed in a 250-ml stoppered, conical flask, treated with 5 ml of 24% potassium dihydrogen phosphate solution and 1.0–1.5 ml of saturated bromine water and allowed to stand stoppered for 5 min. The destruction of the excess bromine and iodometric titration is as described previously[7].

*Total halide determination*

After addition of a known amount of screened indicator to the 20-ml aliquot in a 100-ml conical flask, the solution is neutralised and treated with exactly 10 ml of mercuric oxycyanide solution. The released hydroxyl ions are titrated with 0.01 *N* sulphuric acid (= *a* ml). The chloride is evaluated as described under (*A*).

*Calculations*

Total halide titre = $a$ ml of 0.01 $N$ $H_2SO_4$
mg of $I^-$ found in aliquot = $b$ ml of 0.02 $N$ $Na_2S_2O_3 \times 0.4231$
$Cl^-$ acid equivalent = $(a - b/3)$
mg of $Cl^-$ found in aliquot = $c$ ml of 0.005 $N$ $NaCl \times 0.1773$

### *D. The simultaneous determination of bromine and iodine* (a general method)

*Procedure*

7–8 ml of 1 *N* sodium hydroxide containing 3–5 drops of 35% sodium bisulphite solution are used as absorbent. Excess of bisulphite is removed by boiling the resulting solution with 2–3 drops of M.A.R. 30% hydrogen peroxide. The cooled solution is neutralised with 1 *N* phosphoric acid in presence of aqueous methyl red indicator solution and then diluted to 50 ml in a standard flask. Two aliquots of 20 ml are taken for the separate halogen evaluations.

*Determination of iodine*

The aliquot is placed in a 250-ml stoppered flask treated with 1.0–1.5 ml of saturated bromine water and allowed to stand for 5 min. The subsequent treatment and titration procedure is exactly as described previously. Mg of $I^-$ in aliquot = $a$ ml of 0.02 $N$ $Na_2S_2O_3 \times 0.4231$.

### *Determination of total iodine and bromine*

The 20-ml aliquot is subjected to the hypochlorite oxidation procedure and the total halate is evaluated iodometrically with 0.02 *N* thiosulphate (*b* ml).

### *Calculation*

$$\text{mg of Br}^- \text{ found in aliquot} \doteq (b - a) \text{ ml of } 0.02\ N\ \mathrm{Na_2S_2O_3} \times 0.26639.$$

### *Blank determination*

The blank on all reagents must be checked preferably by burning a sample of benzoic acid or sucrose.

## *E. The simultaneous determination of chlorine, bromine and iodine (in the presence or absence of N and/or S)* (a general method)

### *Procedure*

The sample (10–12 mg) is burned as usual and the combustion products are absorbed in 7–8 ml of 0.1 *N* sodium hydroxide solution containing 3–5 drops of 35% sodium bisulphite solution. After transference to a 100-ml conical flask, excess of bisulphite is destroyed by heating with 1–2 drops of M.A.R. 30% hydrogen peroxide. The cooled solution is neutralised with 0.1 *N* sulphuric acid, using aqueous methyl red as indicator and then made up to 50 ml in a graduated flask.

Three aliquots of 15 ml are required for the evaluation procedures, two being transferred to 250-ml stoppered, conical flasks and the third to a 100-ml conical flask.

The iodine, total bromine and iodine and total halide determinations are then carried out as already described for the di-halogenated combinations. The chlorine is evaluated by the comparison titration procedure after deducting the acid equivalents for bromine and iodine.

## SUMMARY

The absorption of the gaseous combustion products from the rapid, empty tube combustion procedure has been studied. Organic compounds containing any combination of chlorine, bromine, and iodine as well as oxygen, nitrogen and sulphur have been examined. Several methods based on established titration procedures have been developed for the simultaneous microdetermination of any two or all three halogens in organic materials.

## RÉSUMÉ

Les auteurs ont effectué une étude sur l'absorption des produits de combustion gazeux et proposent des méthodes titrimétriques pour le microdosage des halogènes dans des substances organiques, par le procédé de combustion rapide.

## ZUSAMMENFASSUNG

Beschreibung von Titrationsverfahren zur gleichzeitigen Bestimmung verschiedener Halogene in organischen Substanzen nach Verbrennung mit Sauerstoff im leeren Rohr.

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# ON THE CONCENTRATION AND SEPARATION OF THE TRACE ELEMENTS: Fe, Cu, Zn, Mn, Pb, Mo and Co*

## I. ION EXCHANGE METHODS

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(Received September 28th, 1960)

### GENERAL INTRODUCTION

Owing to the increasing demand for rapid results in analytical chemistry, there is a general trend to automation, but at the same time the problems posed become more and more complex. It is thus impossible to do without classical chemical methods and separation techniques, such as ion exchange, solvent extraction and paper chromatography (*cf.* White[1]). This statement is certainly true for trace analysis, where automation is only possible to a very small extent. Only in a limited number of cases (for instance, in some activation methods and in X-ray-fluorescence) is the determination of micro constituents feasible without any classical chemical treatment. Generally, some pretreatment is inevitable, and usually involves concentration of the traces, separation from the macro-constituents and mutual separations. In fact, the development of the separation techniques mentioned above has been greatly stimulated by the importance of trace analysis.

A satisfactory pretreatment should (*1*) concentrate the trace elements to a level at which they can be determined with the accuracy required, (*2*) separate the ions to be analysed from interfering constituents and (*3*) not introduce any compound interfering with the subsequent quantitative determination(s). In some radiochemical separations, a rapid method is required, owing to the short half-lives of the nuclides concerned.

This study is restricted to ion exchange (part I), solvent extraction (part II) and paper chromatography (part III), the results being compared at the end of part III. Elegant solutions of the problem are of course also offered by other methods, but none of these techniques has been so generally accepted as the three mentioned above (*cf.* Norris[2]; Cooke[3]). Precipitation must be rejected because of the adsorption-, occlusion- and coprecipitation-effects involved.

A further restriction is made to the ions of iron(III), copper(II), zinc(II), manganese (II), lead(II), molybdate and cobalt(II), while sodium, potassium, calcium, magnesium, phosphate and sulfate ions are considered to be macro-constituents (this classification refers to the situation in the animal field. Application of our results to other fields is of course possible in many cases).

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* Publication No. 128ª of the Research Institute for Animal Husbandry "Schoonoord", Hoogt 10bis, Utrecht (The Netherlands).

Separations are primarily considered in connection with radiometric determinations of the trace elements, but they are also applicable to other quantitative techniques.

## INTRODUCTION TO ION EXCHANGE STUDY

Many new techniques have been developed since RICHES[4] and LUR'E AND FILIPPOVA[5] carried out their experiments on the concentration of trace elements by ion exchange. Apart from more efficient concentration techniques, separations of many inorganic ions have been developed. Reviews have been given by ABRAHAMCZIK[6], KRAUS[7], KUNIN[8,9] and HUDGENS[10].

Three different approaches to the problem can be distinguished*:

*(1) Specific ion exchange materials* were developed as a parallel to the natural occurring specific metal-complexes. SPECKER *et al.*[11,12] separated iron(III) from other cations and also separated Cu, Zn, Mn, Pb, Co, Ca and Mg from alkali metals; CORNAZ AND DEUEL[13] devised a selective method for iron(III); BAYER[14] obtained a separation of copper and cobalt from zinc, magnesium and barium; KULČICKYJ[15] prepared a selective exchange material for copper. GRIESSBACH[16], TROSTYANSKAYA AND TEVLINA[17] and KUNIN[18] have reviewed the field.

Future developments will be of considerable interest but a solution to our problem on this basis seemed to be rather improbable.

*(2) Specific complexing agents*, added either to the sample solution, to the eluant, or to the column itself, have been used by many authors and remarkable results have been obtained, *e.g.* in the separation of the rare earth elements. Unfortunately, many complexes interfere with (most of) the subsequent quantitative determinations and thus one of the major advantages of ion exchange is lost. The negatively charged chloro-, bromo-, and fluoro-complexes do not suffer from this disadvantage. A separation of many metals by anion-exchange of their chloro-complexes is possible, as was shown by MOORE AND KRAUS[19]. A review of the extensive literature with Dowex 1 X 10 has been given by KRAUS AND NELSON[20] while results with Wofatit-150 have been reviewed by JENTZSCH[21]. Alcohol-hydrochloric acid mixtures were used by WILKINS *et al.*[22] and by BERG AND TRÜMPER[23]. Unfortunately, with the ashes of biological samples, precipitates of the major constituents are obtained in concentrated solutions of chloride or bromide, thus this method can only be used when the major constituents have been previously removed.

*(3) Specific elution of cation-exchange columns with organic solvents* has been practised by only a few authors: KEMBER *et al.*[24] separated copper from iron and nickel on Zeocarb 225-H with mixtures of acetone, hydrochloric acid and water. Later these authors[25] recommended Amberlite IR-112. IONESCU *et al.*[26] and BUZNEA *et al.*[27] separated copper and zinc with a similar solvent on the ion-exchange materials KU-2 and R-21.

As this method does not suffer from the disadvantage mentioned above, it was chosen for our experiments. Radioactive tracers were used to facilitate the evaluation of the results.

## EXPERIMENTAL

### *Materials*

*Choice of the resin.* Many resins collapsed in the elution mixtures. Amberlite IR-112 and Amberlite XE-100 (which according to the manufacturer, Rohm and Haas, Philadelphia (U.S.A.), have the same properties) were the most satisfactory.

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* Other ion exchange procedures, *e.g.* electro ion exchange are not considered here.

*Chemicals (not radioactive).* Ion exchange water was used, which had a resistivity of at least 3 Megohms. The sulfuric, perchloric, hydrochloric and nitric acids and the ammonia were of "AnalaR" quality and had specific gravities of 1.84, 1.54, 1.18, 1.42 and 0.88 respectively. Nitrates and chlorides were used for the inorganic salts; all reagents, including: sodium pyrophosphate, disodium phosphate, hydrogen peroxide (30%), potassium iodide, hydrazine hydrate, methanol, ethanol, chloroform, acetone (containing 1% water), rubeanic acid and titan yellow, were of reagent grade (either AnalaR or Merck *p.a.*).

*Radio-active chemicals.* Dilutions from a small volume to 1 ml are given and (between brackets) the amounts of the anion or metal used per experiment (in ml, m$\mu$C and $\mu$g respectively; for molybdenum, which has a short half life, a medium value for the amount in $\mu$g is given).

$^{35}SO_4^{-2}$: 66 $\mu$C $Na_2{}^{35}SO_4$ (carrier free) in water, diluted with 0.01 $M$ sulfuric acid to 1 ml (0.001–66–0.5).

$^{32}PO_4^{-3}$: 17 $\mu$C $Na_2H^{32}PO_4$ (carrier free) in water, diluted with 0.01 $N$ phosphoric acid to 1 ml (0.001–17–0.33).

$^{59}Fe$: 150 $\mu$C $^{59}Fe^{+3}$ (33 $\mu$g) in 1 $N$ hydrochloric acid, diluted with the same acid to 1 ml (0.001–160–0.05).

$^{65}Zn$: 200 $\mu$C $^{65}Zn^{+2}$ (1000 $\mu$g) in 1 $N$ hydrochloric acid, diluted with the same acid to 1 ml (0.001–200–1).

$^{210}Pb$: 100 $\mu$C $^{210}PbCl_2$ (Radium-D in equilibrium with its decay products) in 2.5 $N$ nitric acid, diluted with 9 $N$ hydrochloric acid to 7 ml; 210 $\mu$g of inactive lead was added, the decay products were removed by anion-exchange through a 5-ml column of Dowex 1 X 10, and the eluate was diluted with 9 $N$ hydrochloric acid to 10 ml (0.1–1000–0.22)*.

$^{99}Mo$: 30 $\mu$C $(NH_4)_2{}^{99}MoO_4$ (2500 $\mu$g Mo) in water, diluted with water to 1 ml (0.005–150–12.5).

$^{54}Mn$: 10 $\mu$C $^{54}MnCl_2$ (carrier free) in 0.1 $N$ hydrochloric acid, diluted with 1 $N$ hydrochloric acid to 1 ml (0.01–100–$10^{-5}$).

$^{60}Co$: 100 $\mu$C $^{60}Co^{+2}$ (10 $\mu$g) in 1 $N$ nitric acid, diluted with this acid to 1 ml (0.001–100–0.01).

$^{89}Sr$: 1.25 $\mu$C $^{89}SrCl_2$ (carrier free) in 0.1 $N$ hydrochloric acid, diluted with $N$ hydrochloric acid and 10 mg of Sr as $SrCl_2$ added (0.001–800–10).

$^{45}Ca$: 0.25 $\mu$C $^{45}Ca^{+2}$ (0.2 $\mu$g) in 0.1 $N$ hydrochloric acid, diluted with 1 $N$ hydrochloric acid (0.1–26–0.02).

### *Apparatus*

The *column* consisted of a pyrex glass tube (Fig. 1), fitted with a removable funnel (A) and a fused-in filterplate (B).

*Measurement of radio-activity* was performed with an end-window GM-tube (Philips 18506), a GM-tube for liquid samples (20th Century Electronics M-6) or a well-type NaI-crystal (Philips PW 4111/W), all combined with a scaler (Philips 4022-32-52). With the crystal sometimes a single-channel analyzer was applied (E.K.A.F. 30301-20102).

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* For details see ref.[28]

*Further apparatus:* Beckmann-DU spectrophotometer with flame attachment; Photovolt densitometer with scanning attachment; Beckmann-G pH-meter.

*Wet ashings* were performed with the apparatus shown in Fig. 2. The pyrex glass tubes (A) were cleaned with sulfuric–chromic acid and then with 3% hydrofluoric acid and were kept under 2 *N* nitric acid. These tubes were heated on the aluminium case (B) over an infrared heater (C), fitted with a mirror (D). Reagents were added through (E) and vapors removed through (F).

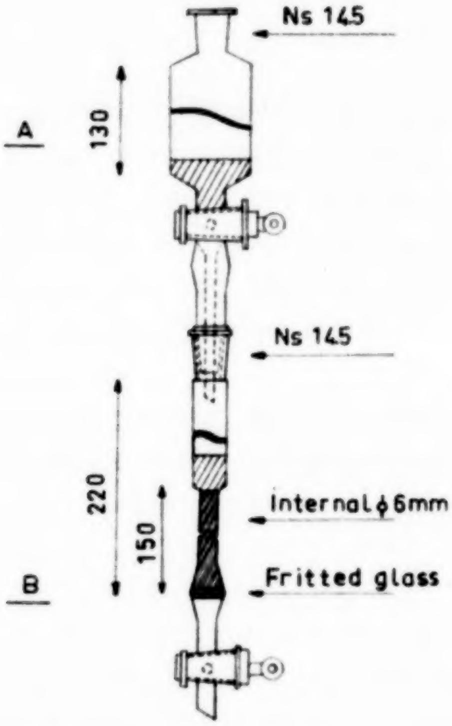
Ns 145
A
130
Ns 145
220
150
Internal ϕ 6mm
Fritted glass
B

Fig. 1. Ion exchange column.

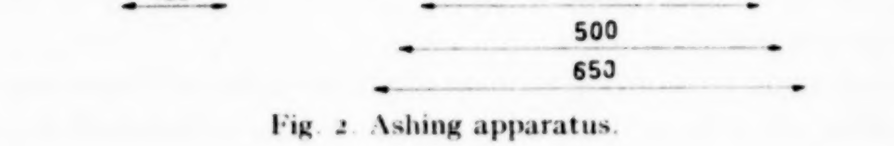
E
F
glass
150
70
A
30
100
C
B
D
120
40
20
E
F
glass
A
B
C
AL
400
500
650

Fig. 2. Ashing apparatus.

*Pretreatment of the ion-exchange column and the sample*

The ion-exchange material was treated with 0.5 *N* hydrochloric acid and added to the column as a slurry. After a final wash with 10 ml of the 0.5 *N* and acid 10 ml of water, it was ready for use.

The length of the column depended on the amount of cations to be analysed. As the capacity of the wet resin is about 2 milliequivalents per ml and the column can be loaded with cations to about 20% of its capacity, a column of 15 cm (4 ml) is sufficient for 1.6 milliequivalents of cations (or for the ash of 3 g of dry cow liver or 0.8 g of dry grass for instance).

About 1 g of the air-dried sample was ashed with 0.5 ml of sulfuric acid and some nitric acid. Either hydrogen peroxide or perchloric acid was used to clarify the solution. The latter reagent was only added when the mixture contained no coarse particles. After cooling, the solution was diluted with water to 100 ml and added to funnel A of Fig. 1.

### *Separation technique*

The solution of the ash in general had a pH between 1 and 2. Although this value is rather low for sorption by cation-exchange material, it was not increased owing to possible losses of iron(III) at higher pH values. SAMUELSON[29] reported such losses and ascribed them to the formation of colloidal hydroxide*.

Our own experiments, carried out with the ash of 1 g of dry cow liver containing about 300 $\mu$g of iron(III) in 100 ml, denoted a loss of: 0, 0.5, 10 and 25% at pH 2.0–2.5, 3.0 and 3.5 respectively.

Sorption was carried out slowly (a flow rate of 10 ml/min/cm$^2$) in order to obtain homogeneous loading of the column and sharp separations. The last traces of the anions were washed out with 0.01 $N$ hydrochloric acid in order to keep the iron(III) adsorbed on the column.

*Before the separation* (with the acetone–hydrochloric acid mixtures) the column had to be adjusted to the right acetone concentration with a mixture of acetone and water. Gas bubbles were formed during this treatment (by evaporation of the acetone) but their influence on the efficiency of the separation proved to be small. A cold-water jacket can be used to minimize this effect.

Mixtures of several of the lower esters, alcohols and ketones with aqueous solutions of hydrohalic acids were investigated for the *selective elution*. Acetone–hydrochloric acid was found to be the most satisfactory .Separation into the groups, Fe, Cu, Zn, Pb — Co, Mn — Na, K, Ca, Mg was achieved with acetone–hydrochloric acid mixtures of different composition. The separation of copper and cobalt was the most difficult; separation was obtained more rapidly with a solvent containing acetone–hydrochloric acid–0.01 $N$ potassium iodide (89 : 1 : 10) to which some hydrazine was added to prevent oxidation. The excess of iodide interfered with most subsequent quantitative determinations, hence it had to be oxidised and the iodine boiled out, which made the method more complicated.

With 15-cm columns, 100 ml of acetone–hydrochloric acid was required for each elution; a velocity of 3 to 4 ml/min/cm$^2$ had to be maintained to achieve sharp separations.

The eluates were collected in "Teflon" dishes and before analysis the acetone was evaporated in a clean atmosphere. The columns were regenerated with 2 $N$ hydrochloric acid, which eluted Na, K, Ca, Sr, Ba and Mg, and were finally washed with water.

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* The difficulties encountered by HAMM[30] in the sorption of iron(III) were due to the formation of excessive amounts of pyrophosphate in his dry-ashing technique. In wet-ashing only traces of this anion are formed.

*Analytical methods*

The efficiency of the separation was tested:

(*1*) *With radio-isotopes (see Materials, p. 44).* $^{45}$Ca and $^{35}$S were measured with the end-window GM-tube, $^{89}$Sr and $^{32}$P with the M6 GM-tube and the other isotopes with the scintillation counter. With the aid of the single channel analyser several isotopes could be measured simultaneously. All measurements were performed in solution, except for the fractions containing $^{45}$Ca or $^{35}$S which had to be evaporated in an aluminium dish.

(*2*) *Magnesium* was determined with titan yellow following SANDELL[31]. For *copper* a densitometric method with rubeanic acid was preferred as it allowed the measurement of a large number of samples (parts of the eluates) in one procedure*.

Strips of Whatman No. 1 paper (2.5 × 50 cm) were washed** chromatographically in the descending way with (*a*) 9:1 methanol–hydrochloric acid, (*b*) 9:1 methanol–ammonia and (*c*) 95:5 methanol–water, each washing lasting 24 h. The washed paper had a copper-content of less than 0.01 μg/cm$^2$ as was determined by ashing two strips and applying the determination described below.

With a micropipet 0.01 ml of the eluate of the ion-exchange column (or its concentrate***) was placed on a washed paper strip, dried for 2 h, neutralized by placing for 1 h in ammonia vapor and sprayed with a 0.5% solution of rubeanic acid in ethanol on both sides. The spray was of an ordinary type, the current of air being delivered automatically in order to obtain a steady stream of the reagent. The paper strip was moved by hand, but as continuously as possible, before the sprayer at a distance of about 20 cm. This spray was repeated 2 or 3 times. The dried spots were measured with the Photovolt densitometer, a slit of 0.1 × 0.6 cm and a color filter with a maximum at 630 mμ being used. Beer's law was followed from 0.1 to 2.0 μg of copper/0.01 ml.

When standards were placed between the samples the standard deviation was 8% and 4% for the ranges of 0.1–1.0 and 1.0–2.0 μg of copper respectively. Microgram amounts of cobalt and nickel interfered; a reagent-blank had to be subtracted.

(*3*) Finally, *sodium and potassium* were analysed by flame photometry, with which less than 0.004 and 0.2 μg per ml of the respective elements could be determined.

## RESULTS

The figures given in Tables I, II and III were all found as a mean of 4 experiments with the ash of 1 g of dry cow liver. Table I shows the separation of cobalt from Cu, Fe, Zn and Pb (manganese behaves similarly to cobalt). It is clear that the mixture 93–1–6 is to be preferred (the acetone contained an additional 1% of water).

Table II shows the separation of cobalt and manganese from calcium (the other alkaline earth metals behaved similarly and the alkali metals slightly better). It is clear that the mixture 93-5-2 is to be preferred. Table III shows the complete separation with the mixtures selected above.

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* A similar method using either 8-hydroxyquinoline or 7-iodo-8-quinolinol-5-sulfonic acid proved to be suitable for the determination of 0.1 μg of iron in 0.01 ml: a 1% solution of the reagent in ethanol–chloroform (1:1) and a color filter with a maximum at 570 mμ were used. When more than a few mg of sulfate or phosphate was present per ml, the latter reagent is to be preferred (see also ZIEGLER[32]).

** The choice of this purification method was justified in a more extensive consideration of the problem[28].

*** Concentrated in a "Teflon" dish, by evaporation, following the method of THIERS *et al.*[33].

TABLE I

SEPARATION OF Co FROM Cu, Fe, Zn AND Pb

(Percentages found in the first acetone–hydrochloric acid–water eluant)

| *Metal* | *Eluant*[a] | | | | | |
|---|---|---|---|---|---|---|
| | *89-1-10*[b] | *89-1-10* | *91-1-8* | *92-1-7* | *93-1-6* | *94-1-5* |
| Co | 0.0 | 0.1 | 0.3 | 0.4 | 1.4[c] | 36.5 |
| Cu | 99 | 77 | 89 | 96 | 98 | 99 |
| Fe, Zn, Pb[d] | 99 | 94 | 96 | 98 | 99 | 100 |

[a] Volume percentages of acetone, hydrochloric acid and water respectively.
[b] 10% 0.01 *N* potassium iodide instead of water.
[c] Standard deviation 0.5.
[d] Mean values for the 3 elements are given.

TABLE II

SEPARATION OF Mn AND Co FROM Ca

(Percentages found in the second acetone–hydrochloric acid–water eluant)

| *Metal* | *Eluant*[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *98-1-1* | *97-1-2* | *96-2-2* | *95-3-2* | *94-4-2* | *93-5-2* | *92-6-2* | *92-5-0* |
| Mn | 79 | 76 | 86 | 90 | 93 | 94 | 94 | 96 |
| Co | 90 | 89 | 93 | 94 | 95 | 97 | 97 | 98 |
| Ca | 1.5 | <1 | 1.5 | 1.5 | 2.0 | 2.5[b] | 3.0 | 3.5 |

[a] Volume percentages of acetone, hydrochloric acid and water respectively.
[b] Standard deviation 0.6.

TABLE III

COMPLETE SEPARATION OBTAINED BY CATION-EXCHANGE

(in percentages)

| *Fraction*[a] | *Ion* | | | *Ion* | | | | *Ion* | | *Ion* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $MoO_4^{-2}$ | $SO_4^{-2}$ | $PO_4^{-3}$ | $Fe^{+3}$ | $Zn^{+2}$ | $Pb^{+2}$ | $Cu^{+2}$ | $Co^{+2}$ | $Mn^{+2}$ | $Ca^{+2}$ | $Mg^{+2}$ | $Sr^{+2}$ |
| First effluent | 96 | 96 | 96 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Washing liquid | 2 | 3 | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 93-1-6 | <1 | <0.5 | <0.5 | 99 | 99 | 99 | 98 | 1.5 | 1.0 | 0 | 0 | 0 |
| 93-5-2 | | | | <0.5 | <0.5 | <0.5 | 2.5 | 97 | 94 | 2.5 | 1.5 | 2.0 |
| 2 *N* HCl and $H_2O$ | | | | | | | | <1 | 4 | 97 | 98 | 98 |

[a] See procedure below; the 93:7 acetone–water contained none of the ions to an appreciable extent; less than 0.5 or 1.0% of the respective ions was found in the column after the final treatment with 2 *N* hydrochloric acid and water.

## CONCLUSIONS

(*1*) The most important separations: Fe-Mn; Fe-Mo; Fe-Co; Cu-Co and Mn-Zn are all established. The trace elements are separated from the macro constituents and concentration is easily accomplished. No interfering complexes are introduced.

(*2*) Further separations of the groups Co-Mn and Fe-Cu-Zn-Pb are possible, *e.g.* by applying anion exchange to the evaporated eluants (concentrated hydrochloric acid).

(*3*) The solvent 93 : 1 : 6 acetone-hydrochloric acid-water (in fact 92-1-7) is better suited for the separation of copper and cobalt than that used by **Kember** *et al.*[24,25] (89 : 1 : 10 of the same constituents), which is however excellent when potassium iodide is added to the water to give a 0.01 *N* solution.

(*4*) The behaviour of the molybdate is in contradiction with the results of **Samuelson**[29].

### *Recommended procedure*

Wet-ash 1 g of air-dried material with 0.5 ml of sulfuric acid and an adequate amount of nitric acid using hydrogen peroxide or perchloric acid if necessary. Cool, and dilute to 100 ml. Fill the column (Fig. 1) with a slurry of Amberlite XE-100 in 0.5 *N* hydrochloric acid and wash with 10 ml of the 0.5 *N* acid and 10 ml of water successively. Adsorb the cations during 40-50 min (molybdenum is found in the eluate) and wash with 50 ml of 0.01 *N* hydrochloric acid during 20 min. Condition with 10 ml of 93 : 7 acetone-water during 5 min and elute Fe, Cu, Zn and Pb with 100 ml of 93 : 1 : 6 acetone-hydrochloric acid-water during 100-125 min. Elute Co and Mn with 100 ml of 97 : 5 : 2 acetone-hydrochloric acid-water over a similar period and regenerate with 20 ml of 2 *N* hydrochloric acid and 20 ml of water (eluting Na, K, Ca, (Sr, Ba) and Mg).

## ACKNOWLEDGEMENT

The author's thanks are due to Mrs. G. A. **Ovezall-Klaasen** for valuable technical assistance.

## SUMMARY

Cation-exchange materials and selective elution with acetone-hydrochloric acid mixtures are used to concentrate the constituents of biological ashes and to separate them into the groups: $MoO_4^{-2}$, $SO_4^{-2}$, $PO_4^{-3}$; $Fe^{+3}$, $Zn^{+2}$, $Pb^{+2}$, $Cu^{+2}$; $Co^{+2}$, $Mn^{+2}$; $Na^{+}$, $K^{+}$, $Ca^{+2}$, $Mg^{+2}$.

## RÉSUMÉ

Au moyen des échangeurs de cations et par des élutions sélectives, il a été possible de concentrer et de séparer divers constituants des cendres biologiques (Fe, Zn, Cu, Mn, Pb, Mo, Co).

## ZUSAMMENFASSUNG

Es wird die Anwendung von Kationen-austauschern und selektive Eluierung mit Aceton-Salzsaure Gemischen beschrieben zur Konzentrierung und Trennung der Bestandteile biologischer Aschen in folgende Grüppen: $MoO_4^{-2}$, $SO_4^{-2}$, $PO_4^{-3}$; $Fe^{+3}$, $Zn^{+2}$, $Pb^{+2}$, $Cu^{+2}$; $Co^{+2}$, $Mn^{+2}$; $Na^{+}$, $K^{+}$, $Ca^{+2}$, $Mg^{+2}$.

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# ANALYSIS OF ARSENIC-IRON ALLOYS

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(Received December 11th, 1960)

## INTRODUCTION

The most accurate method available for the determination of arsenic is probably the titration of As(III) to As(V) with iodine[1]. Indirect iodimetry, the thiosulphate titration of the iodine liberated by iodide ion reduction of As(V) to As(III), is capable of almost equally good results under proper conditions[2]. In order to apply either method to the analysis of arseniferous materials, it is necessary in the practical case to separate the arsenic from the other constituents of the sample. The most generally applicable method of separation is distillation of the arsenic as $AsCl_3$, but as a considerable number of accurate analyses of specially prepared arsenic compositions was required for an X-ray diffraction study of various arsenides, a more expeditious and convenient method was desirable. Separation of the arsenic by ion-exchange as described by ODENCRANTZ AND RIEMANN[3], makes it possible to avoid the distillation altogether and to use the eluate direct from the resin-bed, after pH adjustment, for the titration of the arsenic. These authors obtained the arsenic in the insecticides, which were the subject of their investigation, as $H_3AsO_4$ by dissolving the sample in $HNO_3$ and adding $KBrO_3$ before taking to dryness. On taking up with water and HCl sufficient to give a solution 0.3 $N$ in acid and passing through a column of cation-exchange resin in the H-form, they recovered the As(V) in the eluate, all cations present being retained on the resin. The eluate was then made 4 $N$ in HCl and the As(V) determined by indirect iodimetry with KI and thiosulphate.

The procedure just outlined above was adapted to the analysis of alloys of arsenic with cobalt, copper and nickel. Very satisfactory results were obtained. However, when alloys of arsenic with iron were analyzed by the same method, erratic results were obtained. The sum of the arsenic and iron values was invariably less than 100%. The investigation of this interference and the development of a satisfactory procedure for the rapid analysis of iron-arsenic alloys are the subjects of this report.

## EXPERIMENTAL

### *Reagents*

*Ion-exchange resin.* Most of the work was carried out with Dowex 50 W-X8 Analytical Grade 50–100 mesh, Dow Chemical Company. A few tests were repeated on Amberlite IR 120, Analytical Grade, Rohm and Haas Company.

*Arsenic standard solution.* A 0.1 $N$ sodium arsenite solution was prepared by dissolving 4.9455 g of A.R. grade $As_2O_3$ in 40 ml of 1 $N$ NaOH solution and diluting to about 900 ml. The solution was made neutral to litmus with HCl and diluted to 1000 ml. The final solution was standardized against N.B.S. Primary Standard $As_2O_3$ No. 83b by means of an iodine solution in the usual way.

*Iron standard solution 1 ml = 0.005 g Fe.* Pure iron wire for Standardizing, A.C.S. reagent, was dissolved in 1:1 $HNO_3$ and evaporated to dryness. The residue was taken up with HCl and water and diluted to volume. The solution was standardized gravimetrically and volumetrically by the Zimmerman-Reinhardt method.

*0.1 N Iodine solution.* Prepared in the usual way and standardized against the sodium arsenite solution at frequent intervals, as necessary.

*0.1 N Thiosulphate solution.* Prepared in the usual way and standardized against the freshly standardized iodine solution.

All other reagents mentioned were of analytical reagent quality.

## APPARATUS

The ion-exchange columns were of the conventional pattern made from 10-mm i.d. tubing as shown in Fig. 1. The resin bed was about 10 ml in volume. The 125-ml separatory funnels were marked at 15 ml and 50 ml.

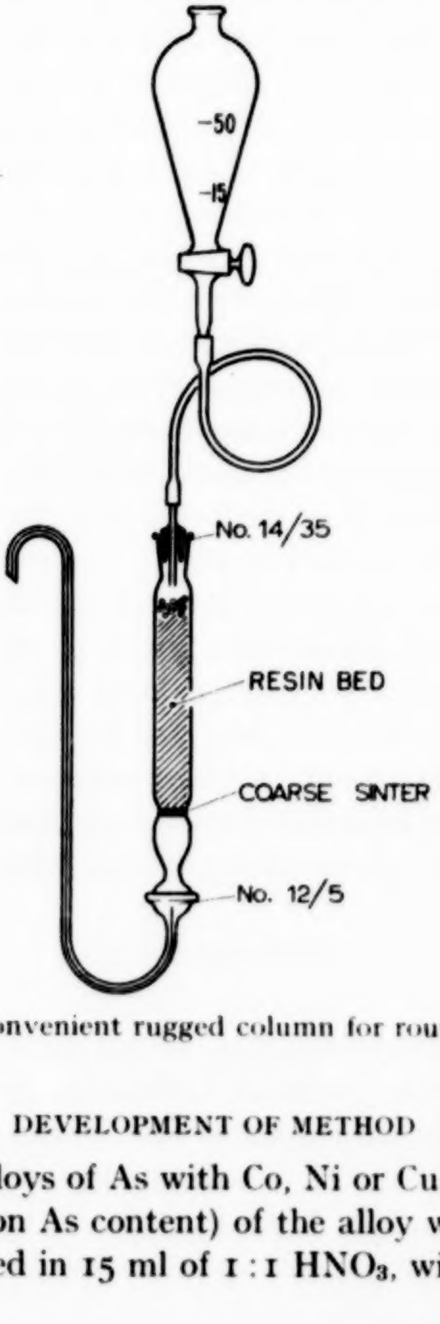

Fig. 1. Convenient rugged column for routine use.

## DEVELOPMENT OF METHOD

*Procedure I*, as applied to alloys of As with Co, Ni or Cu.

About 0.25 g (depending on As content) of the alloy was accurately weighed into a 250-ml beaker and dissolved in 15 ml of 1:1 $HNO_3$, with gentle heating; 10 ml of bromine water was added and the solution evaporated to dryness, finishing on the steam bath. The residue was wetted with about 2 ml of HCl and evaporated again to dryness on the steam bath. This step was repeated once more. The residue was dissolved in 2.5 ml of 1 : 1 HCl and 10 ml of $H_2O$ by gentle warming. When the solution was clear, it was transferred to a separatory funnel marked at 15 ml and 50 ml and made up to a final volume of 50 ml with water. The solution was passed through a column of Dowex 50 W-X8 in the H-form at a rate of approximately 5 ml per min. Three 15-ml portions of 0.3 *N* HCl were then passed through the column, the whole being received in a 500-ml iodine flask. To the nearly 100 ml of eluate in the iodine flask, 60 ml of conc. HCl was added. The solution was cooled to room temperature in a cold water bath and 1 g of $NaHCO_3$ was added in small portions while swirling the solution in the flask. 3 g of KI was added and dissolved and the mixture let stand for 5 min. The iodine was then titrated with 0.1 *N* sodium thiosulphate without added indicator, the final disappearance of the iodine colour being observed against a white background.

The cobalt, copper or nickel on the column was then removed with three 50-ml portions of 2 *N* HCl and determined in any convenient manner.

When As–Fe alloys were treated by this procedure, the iron was determined by precipitation with ammonia and ignition to $Fe_2O_3$. Reasonable concordance of results was obtained for the iron, but the values for the arsenic were erratic and the sum of Fe plus As was significantly less than 100%. This suggested that the As was not completely removed from the column by the washing sequence of *Procedure I* above. With additional washes of 0.3 *N* HCl, more arsenic(V) was in fact recovered from the column containing the Fe(III), but complete recovery was not obtained even after more than 300 ml of 0.3 *N* HCl had been passed through the column (Fig. 2). Further, the Fe(III) had by then begun to near the break-through point.

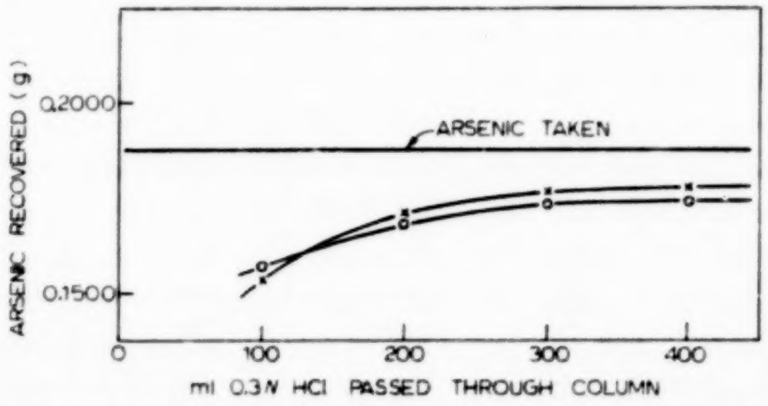

Fig. 2. Recovery of arsenic from synthetic samples containing iron(III) and arsenic(V).

In order to establish that this failure of the $H_3AsO_4$ to pass freely through the resin bed was due to the presence of Fe(III), synthetic samples were prepared from the solutions described above. 50 ml of the standard 0.1 *N* sodium arsenite was heated with 15 ml of $HNO_3$ and bromine water was added till in excess (about 20 ml); 20 ml of the standard ferric iron solution was then added and the whole evaporated to dryness, finishing on the steam bath. After twice moistening with HCl and redrying on the steam bath, the residue was taken up with 2.50 ml of 1 : 1 HCl and about 20 ml of water and transferred to the calibrated separatory funnel where it was finally made to 50 ml with water. This gave a solution of As(V) and Fe(III) in 0.3 *N* HCl which was treated by *Procedure I* above. Low values were obtained for the arsenic (Table I).

TABLE I

RECOVERY OF ARSENIC FROM SYNTHETIC SAMPLES OF Fe(III) AND As(V) WITH STANDARD 100-ml WASH

| *Fe(III) in sample* g | *As(V) in sample* g | *As found* g |
|---|---|---|
| 0.0800 | 0.1874 | 0.1657 |
| 0.0800 | 0.1874 | 0.1625 |
| 0.0800 | 0.1874 | 0.1538 |
| 0.0800 | 0.1874 | 0.1571 |
| 0.0800 | 0.1874 | 0.1532 |
| 0.0800 | 0.1874 | 0.1550 |

TABLE II

RECOVERY OF As(III) AND OF As(V) FROM COLUMNS CONTAINING Fe(II) AND Fe(III) WITH STANDARD 100-ml WASH

| *Fe(II) present in column* g | *Fe(III) present in column* g | *As present as As(III)* g | *As found* g | *As present as As(V)* g | *As found* g |
|---|---|---|---|---|---|
| 0.0800 | | 0.1875 | 0.1875 | 0.1875 | 0.1866 |
| 0.0800 | | 0.1875 | 0.1876 | 0.1875 | 0.1874 |
| 0.0844 | | 0.1875 | 0.1875 | 0.1875 | 0.1873 |
| 0.0844 | | 0.1875 | 0.1874 | 0.1875 | 0.1873 |
| | 0.0800 | 0.1875 | 0.1875 | 0.1875 | 0.1736 |
| | 0.0800 | 0.1875 | 0.1872 | 0.1875 | 0.1721 |
| | 0.0800 | 0.1875 | 0.1875 | 0.1875 | 0.1760 |
| | 0.0800 | 0.1875 | 0.1872 | 0.1875 | 0.1740 |

TABLE III

RECOVERY OF ARSENIC AND IRON FROM SYNTHETIC SAMPLES CONTAINING Fe(II) AND As(III) WITH STANDARD 100-ml WASH

| *Fe(II) in sample* g | *As(III) in sample* g | *As found* g | *Fe found* g | *Total Recovery* % |
|---|---|---|---|---|
| 0.0844 | 0.1875 | 0.1875 | 0.0843 | 99.96 |
| 0.0844 | 0.0937 | 0.0935 | 0.0845 | 99.94 |
| 0.0844 | 0.0562 | 0.0564 | 0.0844 | 100.14 |
| 0.0844 | 0.0375 | 0.0377 | 0.0844 | 100.16 |
| 0.0844 | 0.0188 | 0.0189 | 0.0844 | 100.09 |

Similar standard solutions containing As(V) and Fe(III) were tried on Amberlite 120 and again, incomplete recovery of the arsenic was obtained.

Since the method described as *Procedure I* above had succeeded with cobalt, nickel and copper, all divalent ions, the effect of reducing the iron to the divalent state was next tried.

Table II shows the behaviour of As(V) and As(III) on columns in which iron had previously been deposited. Columns containing Fe(II) permitted complete recovery of both As(III) and As(V); columns containing Fe(III) permitted complete recovery of As(III) but showed the expected incomplete recovery of As(V).

Known samples were then prepared containing As(III) and Fe(II) by reducing the standard solution of ferric iron with $SO_2$ and adding the arsenic(III) as standard arsenite solution. After evaporation to dryness and adjustment to 0.3 *N* as before these solutions were then treated by *Procedure I*. Complete recovery of the As(III) was obtained (Table III).

Thus, it is clear that the ion-exchange separation of pentavalent arsenic from iron is not possible if the iron is in the trivalent state. This specific separation, As(V) from Fe(III), is recommended in a recent text-book of inorganic analysis[4], the paper of ODENCRANTZ AND RIEMANN being cited as source. In fact, ODENCRANTZ AND RIEMANN did not claim to separate As(V) from Fe(III), the only ions mentioned being Cu, Ca, Pb and Mg.

This interference by trivalent iron and not by divalent iron prompted the inclusion of two other trivalent ions, Al(III) and Nd(III) in the synthetic test samples. No interference with the ion-exchange separation in 0.3 *N* HCl solutions of As(V) (as $H_3AsO_4$) from Al(III) or Nd(III) was observed.

From the foregoing, the following relatively rapid procedure was developed for the analysis of iron–arsenic alloys.

### *Recommended procedure for arsenic–iron alloys*

Weigh accurately into a 250-ml beaker sufficient sample to provide about 125 mg of As. Dissolve in 15 ml of 1 : 1 $HNO_3$ by gentle heating. Evaporate the solution to dryness finishing on the steam-bath. Wet the residue with about 2 ml of conc. HCl and again evaporate to dryness on the steam-bath. Repeat this treatment once more. Dissolve the residue in 5 ml of 3 *N* HCl and sufficient water to make the volume about 40 ml. Chill the solution in ice and water and saturate with $SO_2$ gas from a cylinder (Note 1). Allow the closely covered beaker to warm up to room temperature (about 1 h) and expel the excess $SO_2$ by boiling the solution on a hot plate, taking care to maintain the volume by adding water as necessary (Note 2). No odour of $SO_2$ should be detectable above the solution at this point. Cool the solution and wash into the dropping funnel adjusting the final volume to 50 ml. Pass the solution through the column of Dowex 50 at a rate of about 5 ml per min, receiving the percolate in a 500-ml iodine flask. Pass 50 ml of 0.3 *N* HCl through the column in at least three portions so as to wash the funnel adequately into the column. To the 100 ml of solution in the iodine flask add 4 g of $NaHCO_3$ a little at a time (Note 3). Observing the solution against a white background, titrate with 0.1 *N* iodine solution to the first detectable yellow tinge (Note 4).

Elute the iron from the column with about 150 ml of 2 *N* hydrochloric acid and determine it gravimetrically or by the Zimmermann-Reinhardt titration.

### *Notes on the method*

(*1*) Sulfur dioxide is the preferred reductant as it avoids the introduction of any other cation into the solution. However, in order to insure the complete reduction of the arsenic(V) the $SO_2$ concentration in the solution must be maintained at saturation[5]. By chilling the solution to 0° before saturating with $SO_2$, saturation is maintained as the temperature rises.

(*2*) If the volume is allowed to diminish appreciably, the increase in HCl concentration gives rise to the danger of loss of $AsCl_3$.

(*3*) This amount of $NaHCO_3$ provides for the neutralization of the HCl present and about 1.5 g in excess to maintain the desirable alkalinity for the titration.

(*4*) If there is any doubt as to the completeness of reduction, the percolate may be oxidized by taking to dryness with $HNO_3$ and bromine and the arsenic determined as in *Procedure I* above.

This procedure has been applied to numerous alloys of arsenic with iron and a sampling of the results obtained is given in Table IV.

TABLE IV

TYPICAL RESULTS OBTAINED BY RECOMMENDED PROCEDURE

| *Sample number* | *Arsenic* % | *Iron* % | *Cobalt* % | *Nickel* % | *Total* % |
|---|---|---|---|---|---|
| 15 | 72.10 | 27.92 | | | 100.02 |
| | 72.14 | 27.88 | | | 100.02 |
| FM-21 | 57.04 | 42.81 | | | 99.85 |
| | 57.12 | 42.83 | | | 99.95 |
| CAF-3 | 76.12 | 9.82 | 13.94 | | 99.88 |
| | 76.16 | 9.85 | 13.98 | | 99.99 |
| NF-7 | 79.29 | 15.55 | | 5.16 | 100.00 |
| | 79.33 | 15.54 | | 5.19 | 100.06 |

## SUMMARY

Contrary to expectation and to published recommendation it is not possible to separate Fe(III) quantitatively from As(V) on a cation-exchange resin. Ion-exchange can however be utilised for the analytical separation of iron and arsenic if the iron is reduced to Fe(II) before the mixture is passed through the cation-exchange column.

## RÉSUMÉ

Une méthode est proposée pour l'analyse rapide des alliages arsenic-fer. L'arsenic est séparé au moyen d'un échangeur de cations, après avoir préalablement réduit le fer à l'état bivalent, la séparation fer(III) et arsenic(V) n'étant pas possible.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur raschen Analyse von Eisen-Arsen Legierungen. Die Trennung erfolgt mit einem Kationenaustauscher; Eisen muss in zweiwertiger Form vorliegen.

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# CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, USING AQUEOUS ETHANOL AS SOLVENT

## II

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(Received November 4th, 1960)

Complex formation plays an important role in the chromatographic separation of ions as pointed out by POLLARD *et al.*[1,2], who observed that it was essential for the separation of metal ions on filter paper. We have already studied[3-5] the separation of several ions in the presence of varying concentrations of different complexing agents using aqueous alcohol as solvent. In this paper we describe the separation of metallic ions of the same group in the presence of oxalate, tartrate and citrate.

### EXPERIMENTAL

Solutions of the sulphates of iron, aluminium, chromium, zinc, manganese, cobalt and nickel, and of the nitrates of barium, strontium, calcium, magnesium, sodium, potassium and ammonium, and of potassium oxalate, sodium citrate and sodium tartrate were prepared using reagent grade chemicals and standardised by the usual methods. Ascending filter paper strip chromatography as described by GAGE, DOUGLASS AND WENDER[6] was applied. Various concentrations of ethanol were examined but only those which gave good results are recorded here. Series of mixtures were prepared by taking equal concentrations of metals and adding varying quantities

TABLE I

SEPARATION OF METALLIC IONS

| *No.* | *% of ethanol used as solvent* | *Systems investigated (sequence of separation without adding complexing agents)* | *Complexing agent added (equivalents up to which separation is possible)* | | | *Sequence of separation (Complexing agent added)* |
|---|---|---|---|---|---|---|
| | | | $C_2O_4^{-2}$ | *Tart.*$^{-2}$ | *Cit.*$^{-3}$ | |
| 1 | 75 | Cr–Fe–Al | — | 0.35 | 0.48 | Cr–Fe–Al |
| | | | 0.16 to 0.20 | — | — | Al–Cr–Fe |
| 2 | 50 | Co–Mn–Zn | — | 0.32 | 0.32 | Co–Mn–Zn |
| 3 | 75 | Zn, Ni, Mn | 0.20 | 0.96 | 0.40 | Only Zn is separated |
| 4 | 90 | Ca–Sr–Ba | 0.20 | 0.32 | 0.32 | Ca–Sr–Ba |
| 5 | 90 | Mg–$NH_4$–K | 0.32 | 0.32 | 0.32 | Mg–$NH_4$–K |
| 6 | 90 | Mg–$NH_4$–Na | 0.32 | 0.20 | 0.32 | Mg–$NH_4$–Na |

of complexing agent, the total volume being kept constant. The ratio of the total molar concentration of metals to the concentration of the complexing agent is mentioned below. The mixtures were spotted on Whatman filter paper No. 1 and the chromatograms run at constant temperature in a temperature controlled room at 27°. The time allowed for the movement of ions was 1.5 h. In ternary mixtures, the final concentration of each of the metal ions was 0.033 *M*.

Various mixtures [Fe(III), Al(III) and Cr(III); Zn, Mn(II), Ni and Co; Ba, Sr and Ca; Mg, Na, K and $NH_4$] were studied and some of the results are summarised in Table I.

It can be noted that the separation of Fe(III), Al(III) and Cr(III) ions is possible up to the addition of 0.35 and 0.48 equivalents of tartrate and citrate respectively as complexing agent; the sequence of separation is Cr(III)–Fe(III)–Al(III). The sequence of separation becomes Al(III)–Cr(III)–Fe(III) with the addition of 0.16 to 0.20 equivalents of oxalate. The complexing agent was added to the solvent by previous workers but in the present work it was added to the solution of the metal itself. In general, for good separation of the ions, the addition of a complexing agent is essential, otherwise in many cases no satisfactory separation can be obtained. With higher concentrations of the complexing agent than those mentioned above the separation is not possible.

## SUMMARY

The separation of Al, Cr(III), Fe(III), Zn, Mn(II), Ni, Co, Ba, Sr, Ca, Mg, Na, K and $NH_4$ in ternary mixtures with or without the addition of complexing agents (oxalate, tartrate and citrate) by filter paper strip chromatography has been studied with aqueous ethanol as solvent.

## RÉSUMÉ

Les auteurs ont effectué une étude sur la séparation des ions Al, Cr(III), Fe(III), Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg, Na, K et $NH_4$, en présence d'oxalate, de tartrate et de citrate, par chromatographie sur papier, en utilisant des mélanges eau–éthanol comme solvants.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Al, Cr(III), Fe(III), Zn, Mn, Ni, Co, Ba, Sr, Ca, Mg, Na, K und $NH_4$ in Gegenwart von Oxalat, Tartrat und Citrat durch Papierchromatographie mit einem Wasser–Alkohol Gemisch als Lösungsmittel.

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# MICRODOSAGE COLORIMÉTRIQUE DU BORE DANS LES ACIERS PAR L'EMPLOI DU RÉACTIF À L'AZOMÉTHINE H

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(Reçu le 4 octobre 1960)

Le bore introduit dans l'acier en vue d'augmenter la trempabilité se partage au moins entre les trois formes différentes suivantes dont l'existence est très généralement admise: une forme combinée avec l'oxygène, une forme combinée avec l'azote, le reste enfin se trouvant soit à l'état dissous (état souvent dit libre), soit sous forme de combinaison métallique (borure). Il est souhaitable pour le métallurgiste de pouvoir connaître les proportions de chacune de ces trois formes de bore.

Toutes les techniques publiées procèdent en fait de la manière suivante. Après attaque de l'acier par un acide minéral étendu, généralement de l'acide sulfurique ou chlorhydrique à 20% ou 25% en volumes, une partie du bore passe en solution dans l'acide, et il reste une partie insoluble qui est séparée par filtration. On a donc été amené empiriquement à faire une distinction entre le bore soluble et le bore insoluble dans les acides.

Il résulte de l'ensemble des données de la littérature et d'études personnelles, que si le bore insoluble correspond assez sensiblement à la fraction du bore qui est combinée à l'azote, en revanche il n'apparaît qu'une corrélation assez vague entre la teneur en bore soluble et l'augmentation de la trempabilité de l'acier.

Lors de l'attaque de l'acier par un acide étendu, en effet, passent en solution non seulement le bore métallurgiquement actif du point de vue de la trempabilité (bore libre ou à l'état de borure), mais encore le bore oxydé, qui est sans action sur la trempabilité, tandis que seul le bore combiné à l'azote reste inattaqué.

Dans ces conditions, la teneur en bore soluble doit permettre une appréciation d'autant plus significative de l'amélioration de la trempabilité d'un acier que la proportion de bore oxydé est plus faible. C'est pourquoi il a été souvent constaté que la teneur en bore soluble se montre assez étroitement liée à l'amélioration de la trempabilité dans le cas des aciers où l'addition de bore a été faite après désoxydation très poussée du bain (calmage préalable à l'aluminium et au titane en particulier), alors qu'au contraire il n'existe pratiquement aucune corrélation entre la teneur en bore soluble et l'amélioration de trempabilité, si la désoxydation préalable du bain n'a pu être poussée aussi loin, par exemple si le calmage a été fait au moyen de siliciure de calcium.

## DOSAGE DU BORE SOLUBLE ET DU BORE INSOLUBLE DANS LES ACIERS

Le réactif à l'azométhine H[1] a été appliqué au dosage du bore dans les aciers. Il est nécessaire que soient analytiquement éliminés différents éléments gênants dont la présence dans les aciers doit être envisagée comme possible, sinon constante. Outre le fer, on a donc admis que doivent être séparés les éléments suivants: aluminium, titane, vanadium, zirconium, chrome, nickel, molybdène, manganèse, cuivre, etc.

### *Méthode proposée*

Microdosage du bore dans les aciers après extraction des ions gênants au moyen d'une résine échangeuse d'ions.

#### *Domaine d'application*

La présente méthode de dosage convient pour les aciers dont la teneur en bore est inférieure à 0.0500%, c'est-à-dire ceux dans lesquels le bore est introduit pour augmenter la trempabilité. La méthode pourrait cependant être adaptée pour des aciers ayant une teneur en bore plus élevée, soit en prenant une prise d'essai plus faible, soit en prélevant un volume partiel plus faible de liqueur.

#### *Principe*

Après mise en solution de l'acier par de l'acide sulfurique au quart, la liqueur obtenue est filtrée pour séparer le "bore insoluble" du "bore soluble" dans les acides.

*Dosage du bore soluble.* Le filtrat qui contient le bore soluble est étendu avec de l'eau distillée, puis passé sur une résine échangeuse d'ions du type sulfonique, afin d'éliminer certains ions gênants dont le fer, l'aluminium, le titane, le vanadium, le zirconium, etc. Après lavage de la résine, le filtrat est neutralisé, puis concentré. Après filtration sur papier pour éliminer les dernières traces d'éléments gênants restés en solution, la liqueur est complétée à un volume connu. Une partie aliquote de liqueur est prélevée et après addition d'acétate d'ammonium, le pH est amené à 5.2 avec de l'acide acétique. Le réactif à l'azométhine H est alors ajouté et la coloration est développée à l'obscurité.

*Dosage du bore insoluble.* Le filtre qui retient le bore insoluble est incinéré en creuset de platine; puis le résidu est fondu avec du carbonate de sodium. Le culot de fusion est remis en solution par de l'acide sulfurique au quart, et le dosage est continué comme pour le bore "soluble".

#### *Réactifs*

(*1*) Acide sulfurique ($d = 1.83$) au quart (1 : 3); (*2*) Solution d'hydroxyde de sodium 2 *N*; (*3*) Acide acétique pur cristallisable; (*4*) Solution d'acétate d'ammonium à 500 g/l; (*5*) Réactif à l'azométhine H*: azométhine H, 6 g, acide ascorbique, 20 g, eau q.s.p., 1 l; (*6*) Eau distillée obtenue au moyen d'un alambic en cuivre étamé ou mieux d'un appareil distillatoire en silice; à l'exclusion d'eau désionisée obtenue par passage d'eau ordinaire sur des colonnes de résines cationique et anionique; (*7*) Solution titrée de bore: *Solution A* (1 ml = 1 mg de bore). Peser 5.7135 g d'acide borique cristallisé, séché au dessiccateur à acide sulfurique. Dissoudre le produit dans de l'eau distillée et compléter à 1 l en fiole jaugée avec de l'eau distillée. *Solution B* (1 ml = 0.01 mg de bore). Diluer au centième la solution précédente avec de l'eau distillée en s'aidant d'une fiole jaugée; (*8*) Résine cationique Dowex 50, X4, 100–200* (Voir remarques ci-dessous concernant l'emploi de la résine); (*9*) Carbonate de sodium pur anhydre.

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* L'azométhine H étant légèrement hygroscopique doit être conservé en flacons émeri soigneusement bouchés. Il est néanmoins nécessaire de sécher le produit de temps à autre, à l'étuve chauffée à 100–110°, pendant deux heures, et de garder si possible les flacons contenant le produit dans une enceinte (cage vitrée, dessiccateur, etc.) dans laquelle on aura placé une substance desséchante (acide sulfurique concentré, actigel, etc.). Moyennant cette recommandation les résultats obtenus sont très réguliers et reproductibles.

L'azométhine H doit être pesé très exactement.

*Matériel*

(*1*) Appareil pour l'attaque comprenant un ballon de 70 ml avec réfrigérant ascendant à eau relié au ballon par raccord émeri. Le ballon est muni d'un entonnoir à robinet placé latéralement (Fig. 1). Dans cet appareil le ballon, le tube intérieur du réfrigérant, le raccord émeri et l'entonnoir latéral sont obligatoirement en silice; (*2*) Béchers en silice de 600 ml; (*3*) Béchers de 100 ml (de préférence en silice); (*4*) Entonnoirs pour filtres de 70 mm (de préférence en silice); (*5*) Fioles jaugées de 100 ml (de préférence en silice); (*6*) Extracteur en plexiglass (Fig. 1)**; (*7*) Filtres en papier sans cendres (bande bleue) de 70 mm. Avant emploi les filtres seront lavés plusieurs fois avec de l'acide sulfurique à 5% en volume, puis, à fond, à l'eau distillée; (*8*) Creusets en platine de 30 ml.

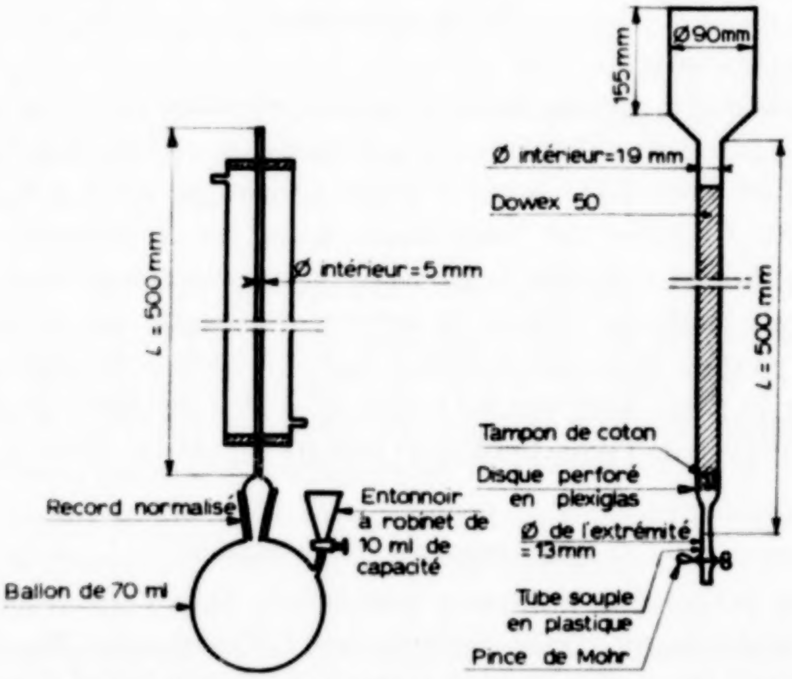

Fig. 1. Appareil pour l'attaque (à gauche). Le ballon, le tube intérieur du réfrigérant, le raccord normalisé et l'entonnoir sont en silice. La gaine extérieure du réfrigérant à eau est en verre ordinaire. Extracteur en plexiglas (à droite).

*Remarques très importantes*

(*a*) Faire très attention aux pertes possibles en bore par entraînement à la vapeur d'eau, en milieu acide.

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* Ou tout autre résine du type sulfonique équivalente à la précédente, ayant même capacité d'échange, même granulométrie, même pourcentage de "cross-linkage", etc.

** Les extracteurs que nous avons utilisés ont été construits par les Etablissements Jahan, 24, Rue des Gravilliers, Paris (3°).

(*b*) à froid (températures inférieures à 30°), les solutions et liqueurs peuvent être manipulées sans inconvénient dans des récipients en verre boro-silicaté. Par contre, à chaud il est absolument indispensable d'opérer dans du matériel en silice. Dès 45°, le verre boro-silicaté introduit des quantités de bore incompatibles avec l'ordre de grandeur des quantités à doser. C'est ainsi que l'acide sulfurique ($d = 1.83$) dilué au cinquième servant à l'attaque sera à préparer obligatoirement dans du matériel en silice.

(*c*) Bien que la verrerie boro-silicatée puisse être utilisée pour les manipulations effectuées à froid, comme il est précisé ci-dessus, il n'est pas moins vrai que l'emploi d'un matériel entièrement en silice (ou à défaut en verre ordinaire exempt de bore) reste cependant beaucoup plus recommandable.

### *Mode opératoire*

Prise d'essai: 1 g ± 0.001.

(*1*) Introduire la prise d'essai dans le ballon en silice de 70 ml de l'appareil d'attaque. Mettre en place le réfrigérant (également en silice). Par l'entonnoir latéral à robinet du ballon introduire 5 ml d'acide sulfurique ($d = 1.83$) dilué au quart. Fermer le robinet. Chauffer au bain-marie à 80° pour attaquer le métal. Après attaque complète, laisser refroidir la solution. Rincer le réfrigérant avec quelques ml d'eau distillée, puis l'enlever. Filtrer la liqueur d'attaque sur un filtre sans cendres (bande bleue) de 70 mm. Recevoir le filtrat dans un bécher en silice de 600 ml. Rincer le ballon et laver le filtre avec environ 150 ml d'eau distillée. Compléter le volume du filtrat à 250 ml avec de l'eau distillée et mettre de côté le filtre qui retient le "bore insoluble".

### *(A) Dosage du "bore soluble"*

(*2*) Verser avec précaution la liqueur précédente dans l'entonnoir d'un extracteur en plexiglass préalablement garni avec 150 ml* de Dowex 50, X4, 100-200. Disposer un bécher en silice de 600 ml sous l'extracteur, et ouvrir le robinet inférieur de l'extracteur de façon que le débit d'écoulement soit de 2-3 ml/min.

(*3*) Quand les dernières portions de liqueur surnageante affleurent le niveau supérieur de la colonne de résine, verser immédiatement avec précaution dans l'entonnoir de l'extracteur 250 ml d'eau distillée et maintenir le débit d'écoulement à la même valeur que précédemment.

(*4*) Après écoulement complet des eaux de lavage, enlever le bécher, et neutraliser le filtrat en versant goutte à goutte une solution d'hydroxyde de sodium 2 *N* (essai à la touche en présence de phénolphtaléine ou d'un papier de tournesol).

(*5*) Evaporer doucement la liqueur (éviter l'ébullition) sur plaque chauffante et concentrer jusqu'à un volume de 50 ml environ. Laisser refroidir.

(*6*) Filtrer la liqueur sur filtre sans cendres (bande bleue) de 70 mm, l'entonnoir qui porte le filtre étant disposé au-dessus d'une fiole jaugée de 100 ml. Rincer le bécher et laver le filtre avec le minimum d'eau distillée. Compléter le volume du filtrat à 100 ml avec de l'eau distillée. Agiter.

(*7*) Prélever 50 ml de cette liqueur et introduire ce volume dans un bécher de 100 ml. Ajouter 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 5.2 avec de l'acide acétique. (Contrôle à l'électrode de verre). Transvaser la liqueur dans une fiole jaugée de 100 ml. Rincer le bécher avec quelques ml d'eau distillée. Ajouter 10 ml de réactif à l'azométhine H et compléter le volume à 100 ml avec de l'eau distillée. Agiter. Laisser la coloration se développer pendant 18 h à l'obscurité, à une température de 20° ± 5°*.

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* Ce qui correspond très sensiblement à 110 grammes de résine humide essorée à fond sur entonnoir de Buchner.

(*8*) Mesurer la coloration, à 415 m$\mu$, par rapport à celle du terme zéro de la gamme d'étalonnage.

### *Tracé de la courbe d'étalonnage du "bore soluble"*

Dans une série de béchers en silice de 600 ml verser 5 ml d'acide sulfurique ($d$ = 1.83) au quart, puis: 0, 1, 2, 3, 4, 5 . . . 10 ml de solution B de bore, correspondant à: 0, 0.0010, 0.0020, 0.0030, 0.0040, 0.0050 . . . 0.0100% de bore dans l'acier pour une prise d'essai d'un gramme. Diluer chacune des solutions à 250 ml avec de l'eau distillée et passer chacune d'elles à travers 150 ml de Dowex 50, X4, 100–200 contenu dans un extracteur identique à celui utilisé pour les essais. Puis continuer comme pour les essais et mesurer la coloration de chacun des termes, à 415 m$\mu$, par rapport à celle du terme zéro de la gamme.

### *(B) Dosage du "bore insoluble"*

(*2'*) Sécher le filtre qui a été mis de côté après séparation du "bore soluble", puis l'introduire dans un creuset en platine de 30 ml. Ajouter sur le filtre 0.500 g de carbonate de sodium anhydre. Chauffer avec précaution pour incinérer le filtre, puis augmenter progressivement le chauffage pour fondre la masse et atteindre une température de 800–1000° qu'on maintient pendant 15 à 20 min. Remuer doucement le creuset pendant ce temps en le tenant avec une pince. Retirer le creuset du feu et le laisser refroidir.

(*3'*) Placer le creuset dans un bécher en silice de 600 ml. Ajouter 10 à 15 ml d'eau distillée et 5 ml d'acide sulfurique ($d$ = 1.83) au quart. Laisser digérer pendant quelques heures (une nuit si possible). Enlever le creuset à l'aide d'une pince et le laver soigneusement à l'eau distillée. Diluer la solution à 250 ml avec de l'eau distillée.

(*4'*) Passer la solution à travers 150 ml de Dowex 50, X4, 100–200 dans les mêmes conditions que pour le dosage du bore soluble; laver la résine avec 250 ml d'eau distillée. Neutraliser le filtrat avec la solution d'hydroxyde de sodium 2 *N*. Concentrer la liqueur à 50 ml environ; filtrer et continuer comme pour le dosage du "bore soluble". Mesurer la coloration finale par rapport au terme zéro de la gamme d'étalonnage.

### *Tracé de la courbe d'étalonnage du "bore insoluble"*

Dans une série de creusets en platine de 30 ml introduire 0, 1, 2, 3, 4 . . . 10 ml de solution B et correspondant à: 0, 0.0010, 0.0020, 0.0030, 0.0040 . . . 0.0100% de "bore insoluble" pour une prise d'essai d'un gramme d'acier. Ajouter 1 goutte de solution d'hydroxyde de sodium 2 *N* (2). Evaporer à sec au bain-marie. Puis introduire dans chaque creuset un filtre de 70 mm identique à celui utilisé pour les essais. Ajouter 0.500 g de carbonate de sodium anhydre. Chauffer avec précaution pour incinérer le filtre, puis augmenter progressivement le chauffage pour fondre la masse et atteindre une température de 800°-1000° qu'on maintient pendant 15 à 20 min environ. Remuer doucement le creuset en le tenant avec une pince. Puis continuer comme pour le dosage du "bore insoluble" (voir ci-dessus). Développer finalement la coloration dans les mêmes conditions que celles indiquées précédemment, et mesurer la coloration de chacun des termes de la gamme, à 415 m$\mu$, par rapport à celle du terme zéro.

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* L'intensité de la coloration est assez sensible à l'influence de la température. Si les conditions précédentes ne peuvent être respectées, il vaut mieux tracer une nouvelle gamme d'étalonnage dont la coloration aura été développée à la même température que celle des essais à mesurer.

*Remarque.* En principe les deux courbes d'étalonnage du "bore soluble" et du "bore insoluble" sont identiques.

*Remarques importantes concernant l'emploi de la résine*

(*1*) Si la résine est neuve, elle doit subir avant tout emploi le traitement préliminaire suivant qui est très important:

(*a*) *Épuisement par de l'acide chlorhydrique au tiers.* Pour 500 g de résine humide placée dans un bécher de 2 l, ajouter 700 ml environ d'acide chlorhydrique ($d = 1.19$) au tiers. Agiter mécaniquement pendant une heure, puis laisser reposer. Décanter l'acide et le remplacer par un même volume d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine, puis laisser reposer et éliminer l'eau de lavage par décantation. Ajouter à nouveau 700 ml environ d'acide chlorhydrique ($d = 1.19$) au tiers et continuer comme ci-dessus. Recommencer 15 fois de suite ce même traitement, au bout duquel l'acide doit être presque incolore.

(*b*) *Traitement alterné au chlorure de sodium et à l'acide chlorhydrique.* Après le dernier lavage à l'eau distillée, verser sur la résine un litre environ de solution de chlorure de sodium à 30 g/l. Agiter mécaniquement pendant une heure. Puis laisser reposer. Vider par décantation la solution qui surnage et la remplacer par un litre d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine. Puis laisser reposer. Décanter l'eau qui surnage et la remplacer par un litre environ d'acide chlorhydrique ($d = 1.19$) au tiers. Agiter mécaniquement pendant une heure, puis laisser reposer. Vider par décantation l'acide qui surnage et le remplacer par un litre environ d'eau distillée. Agiter mécaniquement pendant quelques minutes pour laver la résine, puis laisser reposer. Recommencer deux autres fois le traitement alterné précédent au chlorure de sodium et à l'acide chlorhydrique. En fin d'opération et avant emploi la résine est lavée à fond à l'eau distillée, puis filtrée et essorée à la trompe sur entonnoir de Buchner.

(*2*) *Garnissage de l'extracteur.* (*a*) Dans une éprouvette de 250 ml contenant 100 ml d'eau distillée introduire par petites portions successives une quantité de résine telle que son volume soit sensiblement égal à 150 ml (ce qui correspond à 110 g environ de résine humide).

(*b*) Faire passer peu à peu ce volume de résine dans l'extracteur en l'entraînant par un courant d'eau distillée. Faire très attention à ne pas entraîner de bulles d'air au sein de la masse de résine introduite dans l'extracteur.

(*c*) Quand la totalité de la résine a été introduite dans l'extracteur, attendre quelques minutes pour que la résine se tasse légèrement et prenne sa place. Puis éliminer l'excès d'eau qui surnage en ouvrant légèrement le robinet d'écoulement de l'extracteur. Arrêter l'écoulement quand le niveau de l'eau dépasse de 5 mm environ le niveau supérieur du lit de résine.

(*3*) *Régénération de la résine après emploi.* Bien que cette opération puisse être effectuée directement dans l'extracteur, il est cependant préférable de la réaliser dans un bécher en opérant de la façon suivante: (*a*) Verser 30 ml environ d'eau distillée dans le réservoir de l'extracteur. Secouer l'appareil pour mettre en suspension la partie supérieure du lit de résine. En renversant rapidement le réservoir au-dessus d'un bécher de 2 l, on fait passer dans ce dernier une partie de la résine contenue dans l'extracteur. On répète plusieurs fois de suite cette opération et on arrive ainsi à faire passer peu à peu toute la résine dans le bécher.

(*b*) Quand ce résultat est atteint, laisser la résine se déposer pendant quelques minutes, puis décanter avec précaution l'eau qui surnage.

(*c*) Verser sur la résine environ 500 ml d'acide chlorhydrique ($d = 1.19$) au tiers. Agiter mécaniquement pendant 30 min, puis arrêter l'agitation et laisser la résine se déposer. Décanter l'acide qui surnage et le remplacer par un même volume d'acide chlorhydrique ($d = 1.19$) au tiers. Recommencer 6 fois de suite ce même traitement.

(*d*) Après quoi la résine est lavée à fond six fois de suite avec 500 ml d'eau distillée à chaque fois. On opère comme pour le traitement à l'acide en remplaçant simplement celui-ci par de l'eau distillée. La résine traitée est prête pour un nouvel usage.

(*4*) Si la résine n'est pas utilisée immédiatement elle doit être conservée à l'état humide et de préférence sous de l'eau distillée rendue légèrement chlorhydrique. Comme la plupart des résines cationiques cèdent au bout d'un certain temps une petite quantité de matière soluble colorée en jaune dans l'eau distillée, il est alors nécessaire de relaver à fond la résine à l'acide chlorhydrique au tiers, puis à l'eau distillée au moment de s'en servir.

A titre d'exemple, la Fig. 2 représente la courbe d'étalonnage obtenue pour le bore soluble et le bore insoluble, avec le Spectrophotomètre Jean et Constant, en cuves de 2 cm, à $\lambda = 415$ m$\mu$.

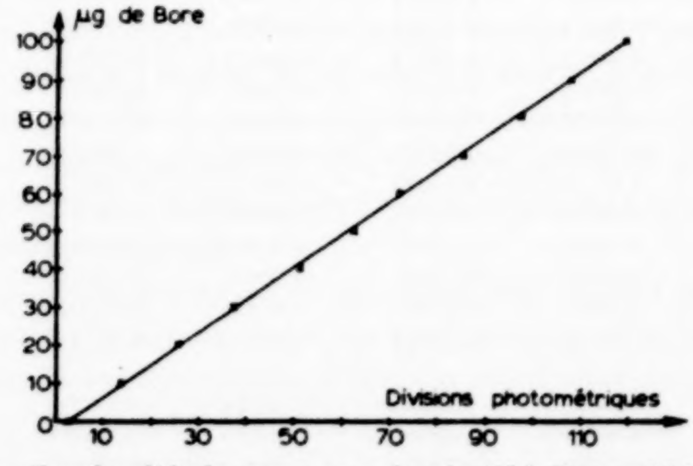

Fig. 2. Courbe d'étalonnage avec le réactif à l'azométhine H.

*Vérification de la méthode*

La vérification de la méthode a été effectuée d'une part à l'aide de divers aciers-étalons, dont la teneur en bore total avait été déterminée par spectrographie, les uns d'origine anglaise de la série des British Chemical Standards (BCS), les autres d'origine américaine, étalonnés par le Bureau of Standards.

L'ensemble des résultats obtenus avec ces aciers-étalons se trouve résumé dans le Tableau I.

## TABLEAU I

| | *Teneur en bore total annoncée (%)* | *Résultats obtenus avec la méthode proposée* | | |
|---|---|---|---|---|
| | | *Teneur en bore soluble (%)* | *Teneur en bore insoluble (%)* | *Teneur en bore total (%)* |
| *Acier-étalon (BCS)* | | | | |
| SS11 | 0.010 | 0.0063 | 0.0039 | 0.0102 |
| SS12 | 0.004 | 0.0032 | 0.0006 | 0.0038 |
| SS13 | 0.002 | 0.0024 | 0.0004 | 0.0028 |
| | | 0.0023 | 0.0005 | 0.0028 |
| SS14 | 0.009 | 0.0089 | 0.0009 | 0.0098 |
| | | 0.0082 | néant | 0.0082 |
| | | 0.0085 (moyenne) | 0.0005 (moyenne) | 0.0090 (moyenne) |
| SS15 | <0.001 | 0.0006 | 0.0002 | 0.0008 |
| SS16 | 0.005 | 0.0025 | 0.0025 | 0.0050 |
| SS17 | <0.001 | 0.0007 | 0.0008 | 0.0015 |
| | | 0.0006 | 0.0010 | 0.0016 |
| *Acier-étalon (Bureau of Standards)* | | | | |
| 425 | 0.0006 | 0.0003 | 0.0005 | 0.0008 |
| 426 | 0.0011 | 0.0008 | 0.0005 | 0.0013 |
| 428 | 0.0059 | 0.0036 | 0.0020 | 0.0056 |
| 429 | 0.0091 | 0.0050 | 0.0044 | 0.0094 |
| 430 | 0.0190 | 0.0116 | 0.0072 | 0.0188 |

## TABLEAU II

| *Acier No.* | *Mode d'introduction du bore dans l'acier* | *Dosage du bore par la quinalizarine* | | | *Dosage du bore par l'azométhine H* | | |
|---|---|---|---|---|---|---|---|
| | | *Bore soluble (%)* | *Bore insoluble (%)* | *Bore total (%)* | *Bore soluble (%)* | *Bore insoluble (%)* | *Bore total (%)* |
| 1301-2 | Grainal 79 | 0.0020 | 0.0005 | 0.0025 | 0.0017 | 0.0006 | 0.0023 |
| 1301-3 | d° | 0.0015 | 0.0005 | 0.0020 | 0.0014 | 0.0003 | 0.0017 |
| 1301-4 | d° | 0.0013 | 0.0002 | 0.0015 | 0.0012 | 0.0003 | 0.0015 |
| 1301-5 | d° | 0.0005 | 0.0003 | 0.0008 | 0.0004 | 0.0003 | 0.0007 |
| 1328 | d° | 0.0018 | 0.0001 | 0.0019 | 0.0021 | 0.0001 | 0.0022 |
| 1331 | d° | 0.0013 | 0.0002 | 0.0015 | 0.0012 | 0.0001 | 0.0013 |
| 1340 | d° | 0.0023 | 0.0001 | 0.0024 | 0.0023 | 0.0001 | 0.0024 |
| 1383-2 | d° | 0.0013 | 0.0005 | 0.0018 | 0.0010 | 0.0002 | 0.0012 |
| 1383-3 | d° | 0.0005 | 0.0004 | 0.0009 | 0.0004 | 0.0002 | 0.0006 |
| 1383-4 | d° | 0.0001 | 0.0003 | 0.0004 | 0.0002 | 0.0004 | 0.0006 |
| 1383-5 | d° | 0.0001 | 0.0003 | 0.0004 | 0.0002 | 0.0003 | 0.0005 |
| 1388-2 | Manganèse bore à 20% | 0.0035 | 0.0044 | 0.0079 | 0.0032 | 0.0036 | 0.0068 |
| 1388-4 | d° | 0.0015 | 0.0020 | 0.0035 | 0.0015 | 0.0022 | 0.0037 |
| 1397-2 | Grainal 79 | 0.0010 | traces | 0.0010 | 0.0010 | 0.0002 | 0.0012 |
| 1400-2 | d° | 0.0010 | 0.0002 | 0.0012 | 0.0010 | 0.0003 | 0.0013 |
| 1421-4 | Laitier boraté | 0.0028 | 0.0022 | 0.0050 | 0.0020 | 0.0027 | 0.0047 |

Ce tableau montre que la teneur en bore total trouvée pour les divers aciers-étalons avec la technique proposée correspond en général bien à celle qui est annoncé sur les certificats d'analyse.

Seuls les résultats trouvés pour les deux aciers-étalons anglais SS13 et SS17 semblent quelque peu élevés; puisque pour des teneurs en bore total annoncées respectivement comme égale à 0.002% et inférieure à 0.001%, il a été trouvé, par des essais faits en double: 0.0028% et 0.0015%; encore faut-il noter que les certificats d'analyse indiquent seulement les unités de la troisième décimale, et ne font nullement mention de la quatrième.

D'autre part, la vérification de la méthode a également été effectuée à l'aide d'un certain nombre d'aciers dont la teneur en bore soluble et en bore insoluble avait été déterminée par la quinalizarine. Les résultats obtenus figurent dans le Tableau II.

A signaler, que les résultats trouvés par la méthode à la quinalizarine d'une part, et par la méthode à l'azométhine H d'autre part, ont été obtenus en partant de prélèvements effectués en deux points différents d'une même barre d'acier laminé. Les différences observées entre les chiffres obtenus par chacune des deux méthodes n'ont rien d'exagéré: elles sont du même ordre de grandeur que les différences normalement observées dans la répartition du bore dans la masse d'acier. On peut donc admettre que les chiffres trouvés par l'une ou l'autre des deux méthodes sont pratiquement identiques.

### *Remarques*

(*1*) *Autre technique envisagée.* Une technique ne faisant pas appel à séparation sur résine échangeuse d'ions avait été envisagée. Son principe était le suivant: après mise en solution de l'acier par de l'acide sulfurique ($d = 1.83$) dilué au cinquième, puis filtration, le filtrat est d'abord électrolysé dans une cellule à cathode de mercure, en silice. Puis, après traitement de la liqueur d'électrolyse par la dithizone et par l'oxine, le "bore soluble" est finalement dosé par le réactif à l'azométhine H.

Pour le "bore insoluble", après incinération du filtre qui retient le "bore insoluble", puis fusion avec du carbonate de sodium, et remise en solution acide, le traitement à la dithizone et à l'oxine est effectué, et finalement le "bore insoluble" est dosé par la réaction à l'azométhine H.

Cette technique s'est montrée à l'expérience assez peu fidèle, une perte de 20% en bore pouvant être observée. Pour cette raison elle ne sera pas développée ici.

(*2*) ***Remarques concernant l'emploi de la verrerie boro-silicatée et le chauffage des solutions contenant du bore.*** Au cours de la présente étude des essais ont été effectués pour déterminer dans quelle mesure la verrerie boro-silicatée peut être utilisée, et, si par chauffage des solutions contenant du bore, il se produit réellement une perte en bore entraînée par la vapeur d'eau.

Les conclusions de ces observations sont les suivantes: A froid, en milieu acide même concentré, le verre boro-silicaté ne cède pas de bore aux solutions. Du matériel en verre boro-silicaté peut donc être envisagé pour la manipulation à froid des solutions. Par contre, par chauffage, il introduit dès 45-50° des quantités de bore absolument prohibitives (plusieurs microgrammes). Du matériel en silice ou en verre rigoureusement exempt de bore doit donc être recommandé. Par chauffage, une quantité assez importante de bore peut être perdue par entraînement à la vapeur d'eau si le pH de la solution boratée que l'on évapore est franchement acide ($pH < 3.7$); en revanche l'expérience a montré que la perte est nulle si le pH est $> 4.9$. Il est donc conseillé de ne chauffer les solutions acides contenant du bore que dans des récipients en silice et sous réfrigérant à reflux.

## DISCUSSION

(*1*) La distinction classique du bore soluble et du bore insoluble étant loin d'être satisfaisante pour l'aciériste, il a été recherché une voie tendant à doser sélectivement la partie du bore soluble qui est combinée au métal sous forme de borure, seul actif sur la trempabilité, à l'exclusion du bore sous forme d'oxyde.

Le dosage des inclusions par la méthode à l'iode alcoolique[2-6] pourrait à la rigueur donner une mesure du bore oxydé, qu'il suffirait de retrancher du chiffre trouvé pour le bore soluble (bore des borures, plus bore oxydé) pour obtenir le bore à l'état libre ou à l'état de borure. Il résulte en fait de plusieurs mesures effectuées par cette méthode de séparation, le bore étant dosé par la méthode à l'azométhine H, que des résultats nets ne peuvent pas être retenus comme valables pour mesurer le bore actif.

(*2*) Des essais tendant à dégager, par attaque en milieu acide et anhydre le bore des borures (bore actif) à l'état de borane, se sont soldés par un échec; ce n'est pas surprenant, vu l'extrême aisance avec laquelle les boranes s'oxydent et s'hydrolysent.

Force est donc d'en rester à la notion classique de bore soluble et de bore insoluble, avec toute l'imprécision que comporte le premier quant à l'action de ce bore sur la trempabilité de l'acier.

## RÉSUMÉ

Le dosage du bore soluble et du bore insoluble dans les aciers est traité au moyen d'une séparation préalable sur résine échangeuse d'ions, suivie de l'application de la réaction colorimétrique à l'azométhine H.

## SUMMARY

A method is described for the determination of soluble and insoluble boron in steels based on preliminary separation with ion-exchange resin and colorimetric determination by means of azomethine-H.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von löslichem und unlöslichem Bor in Stählen durch Behandlung mit einem Austauscherharz und colorimetrische Bestimmung des Reaktionsproduktes mit Azomethin H.

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# CRITICAL FACTORS IN THE COLORIMETRIC DETERMINATION OF SILICA*

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(Received November 21st, 1960)

## INTRODUCTION

During the course of a comprehensive research programme aimed at a better understanding of the controlling factors in the dissolution of natural silicates and the formation of secondary products in aqueous solution under normal temperature and pressure conditions, it became necessary to undertake a large number of determinations for both soluble and total silica. A brief survey of the literature revealed a large number of analytical methods based upon the formation of silicomolybdate complexes. As routine analyses proceeded, it became clear that lack of understanding of controlling factors and the mechanism of formation of these complexes prevented any adaptation of the method to suit the circumstances and still obtain reliable results. Accordingly, an intensive search of the available literature was undertaken, accompanied by detailed experimental work, to determine the optimum operating conditions. Standard commercial reagent-grade chemicals were used throughout, and hence no great accuracy is claimed for the results presented; moreover, the substance of this paper is only a side-issue of a much more comprehensive project. Inasmuch as geological work is now making increasing demands upon chemical and physical techniques, it is felt desirable to record the results obtained.

### *Silica in aqueous solution*

Silica in "solution" exists in a number of different forms: in the pH range 1–8 and in concentrations less than about 110–140 p.p.m., the stable form is the monomeric molecule $Si(OH)_4$[1]; above pH 9 the solubility of amorphous silica rises sharply due to the formation of the silicate ion, thus:

$$Si(OH)_4 + (OH)^- \rightarrow SiO(OH)_3^- + H_2O$$

The silicate ion will exist in solution together with $Si(OH)_4$. At very low pH solubility of silica may be increased by acids, such as HF to form silicofluoride anions. In solutions more concentrated than 110–140 p.p.m. $SiO_2$, polymerization occurs giving rise to polysilicic acids, and ultimately a colloid, gel, or a precipitate. Polymerization of two $Si(OH)_4$ molecules may lead to the formation of dimeric silicic acid where each of the two silicons is surrounded octahedrally by 6 OH ions; further polymerization will lead to the formation of trimeric silicic acid, whilst condensation and elimination of water will lead to branched-chain and ring polymers[2]. Continued increase in size will give rise to the formation of colloidal particles and, under suitable conditions, a gel.

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* Research Council of Alberta, Contribution no. 144.

Iler[2] states that monosilicic acid is most stable at a pH of 1–3, and least stable between pH 5 and 6. According to Alexander[3] monosilicic acid in 0.1 $M$ solution at 2° polymerizes almost instantly at pH 6, and is most stable at pH 3.2; the polymerization below pH 3.2 is a third order reaction, giving linear or openly branched polysilicic acid chains, whilst above pH 3.2 the polymerization is a second order reaction and depolymerization-polymerization rearrangement of polymers gives rise to cyclic or cross linked polymers. Alexander[3] also stated polysilicic acid diluted to 40 p.p.m. depolymerizes at room temperature at a pH of 1.0, but the rate is slow compared with the rate of polymerization. The rate of polymerization at room temperature of polysilicic acid is approximately proportional to the square of the concentration of silica[4].

### *Reaction of silica with molybdic acid*

Dienert and Wandenbulcke[5] in 1923, and Harmon[6] in 1927, showed that only "soluble" silica will react with molybdic acid to form a yellow silicomolybdate complex, and that colloidal silica is unreactive. This reaction has been the basis of very many colorimetric methods for the quantitative determination of silica, either by measurements of the intensity of the yellow silicomolybdate complex or the reduced blue complex. This reaction was further clarified by Weitz, Frank and Schuchard[7] who demonstrated that monomeric silicic acid will react completely in about 75 sec, disilicic acid in about 10 min, whilst higher polymers take even longer. This reaction has been confirmed by Alexander[8] and Richardson and Waddams[9] although, as seen later, it is only true under certain experimental conditions.

In 1952 Strickland[10] published a series of three papers in which he demonstrated that there exists at least two forms of silicomolybdic acid in solution, both having the formula $H_4(SiMo_{12}O_{40})$ and both yellow in color, but having quite different light-absorbances. The stable form was designated as α-silicomolybdic acid which is the predominant form in solutions acidified with up to 1.5 equiv. of acid per mole $MoO_4^{-2}$. The other form, β-silicomolybdic acid, is formed in quantity when more than 1.5 equiv. of acid per mole $MoO_4^{-2}$ is present, and the yellow complex has an absorbance of about twice that of α-complex. The β-acid changes spontaneously to the α-form, a change which is hastened when the pH is raised above 2.5, by heating, and in the presence of excess electrolyte. The change is retarded, even under the latter conditions, when molybdate is present in excess of that required to react with silica. Strickland[10] suggested that the β-acid is an unstable polymer of the α-acid, the spontaneous β to α change having the characteristics of an irreversible depolymerization.

Published analytical methods for the determination of silica have been based upon the formation of the β-acid, although there have been two recent methods[11,12] based upon the formation of the α-complex. Despite Strickland's[10] detailed investigation of the conditions of formation of silicomolybdic acids, his work has been largely ignored or apparently misinterpreted. Most published data place great emphasis upon the pH and give scant attention to the ratio and type of acid to molybdate, nor to the particular species of molybdate added to the reaction — although both of these factors are important as Strickland's[10] work showed. Data are presented in the following paragraphs which confirm or expand some of Strickland's[10] fundamental observations; the conditions to be considered when designing an analytical method for silica to suit particular circumstances are also outlined.

## EXPERIMENTAL RESULTS

It has been asserted by Ringbom *et al.*[11] that pH is the major variable determining the development of the yellow silicomolybdate complexes; these writers published an absorbance-pH curve showing a plateau of constant absorbance values between pH 2 and 4 which they equated with formation of α-silicomolybdic acid. The initial experiments were designed to compare the results obtained by Ringbom *et al.*, who used monochloracetic acid as the acidifying agency, with results obtained when using sulphuric acid. The same concentration of ammonium molybdate recommended by Ringbom *et al.* was used, and the change in absorbance was measured at intervals of 2 min to 96 h over the pH range 0.5 to 5.5.

### *Method*

An aliquot of standard $SiO_2$ solution in a 50-ml volumetric flask was acidified with a suitable mixture of either sulphuric acid and ammonium hydroxide, or mono-

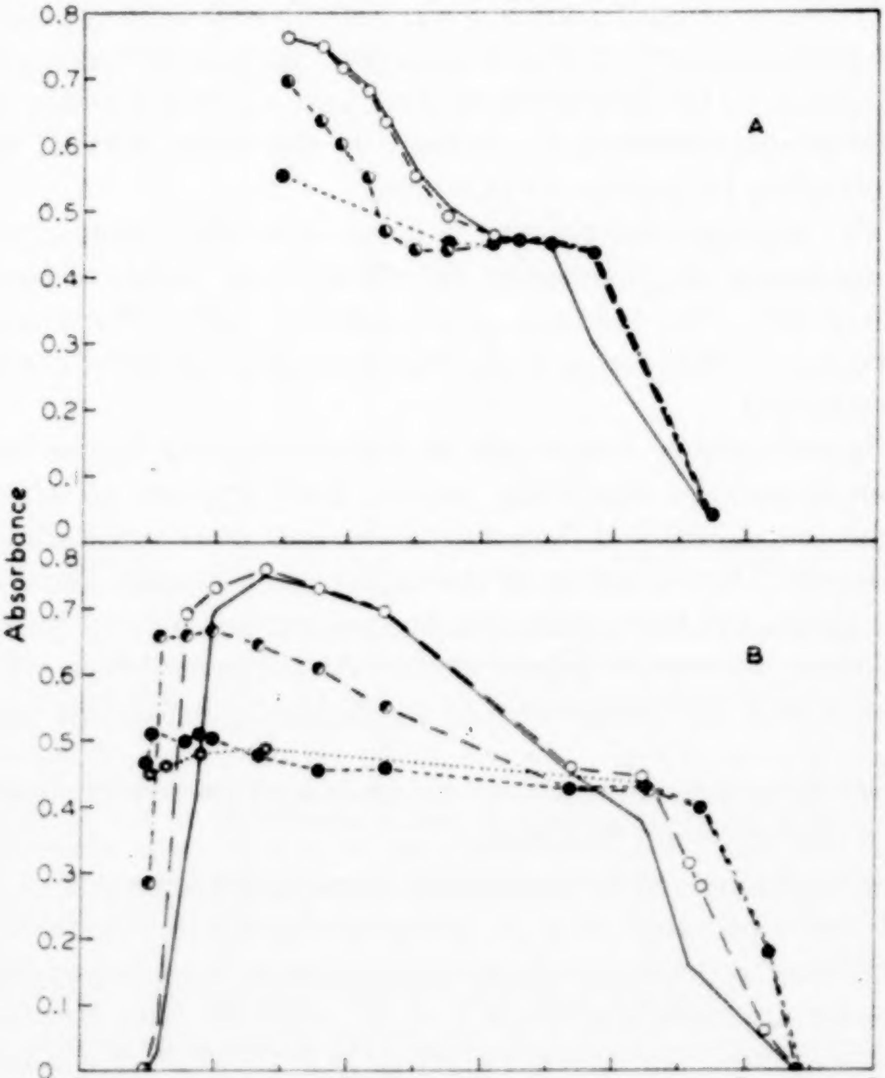

Fig. 1. Variation of absorbance of silicomolybdate solutions due to pH and time, and comparison of results obtained with monochloracetic acid and sulphuric acid. A, solutions acidified by mixtures of 2 *M* monochloracetic acid and ammonium hydroxide. B, solutions acidified by mixtures of 1 *N* sulphuric acid and ammonium hydroxide. ——— absorbance measured 2 min after start of reaction; ○— — ○ absorbance measured 10 min after start of reaction; ◐·–·–◐ absorbance measured 5 h after start of reaction; ● – – – – ● absorbance measured 24 h after start of reaction; ◎ ...... ◎ absorbance measured 48 h after start of reaction.

chloracetic acid and ammonium hydroxide. This was diluted to about 35 ml with distilled water; 10 ml of ammonium molybdate 0.2 *M* with respect to $MoO_4^{-2}$ was added (0.04 *M* strength in reaction), and then diluted to volume with distilled water. The reaction was timed from the addition of ammonium molybdate solution, and the absorbance in this series of experiments measured on a Beckman Model B spectrophotometer at a wavelength of 400 m$\mu$.

Some of the results obtained in this comparative series of experiments are recorded in Fig. 1. The main conclusions to be noted at this stage are:

*1*. When sulphuric acid is used, maximum absorbance is attained within 10 min over the pH range 0.75 to 4.25 (within 2 min at pH 1.75 to 2.25), thereafter decreasing to the same constant value over a period of 48 h, the decrease being most rapid in the more acid range. Above pH 4.75 values increase with time, very slowly above pH 5.0; below pH 0.75 absorbance either continues to increase up to 5 h and then decreases or, at pH 0.5, continues to increase with time.

The maximum values (corresponding to the formation of predominantly $\beta$-silicomolybdic acid) occur between pH 1.0 and 2.5, but with no well defined plateau of constant values; the low plateau observed after 10-min reaction time between pH 3.75 and 4.25 probably corresponds to the formation of dominant $\alpha$-silicomolybdic acid, all higher values at higher acidities tending to decrease to this level, and all lower values at lower acidities tending to increase to this level.

*2*. Whereas the same general pattern is discernible when monochloracetic acid is used, there is one important difference: the whole curve is shifted towards lower pH values compared with that obtained with sulphuric acid. Moreover, the rates of formation and decay of the complexes at any particular pH differ compared with the sulphuric acid reaction.

Clearly, pH is not entirely responsible in determining the formation of the silicomolybdate complexes; the acidifying agency itself appears to affect the rate of formation of the complexes, and the relative amounts of $\alpha$- and $\beta$-silicomolybdic acid at any particular pH. The remainder of the experiments described and reported below were aimed at understanding better the factors controlling the formation of these complexes. All these subsequent experiments were performed with a Beckman Model DU spectrophotometer at a wavelength of 400 m$\mu$ and constant slit width of 0.04 m$\mu$.

### *Variation in absorbance depending upon concentration of ammonium molybdate, and pH of stock solution of ammonium molybdate*

The effect upon the rate of formation and the relative amounts of $\alpha$- and $\beta$-silicomolybdic acid over a pH range of 0.5 to about 5.0 caused by variation in the concentration of molybdate and the pH of the stock solution, was investigated for concentrations of ammonium molybdate from 0.01 *M* to 0.1 *M* with respect to $MoO_4^{-2}$ in the reaction. It was found that unless the pH of the stock solution was kept above about 7.0, reproducible results were not obtained using ammonium molybdate solutions more than 12 h old. Solutions which had a pH of greater than 7.0 (pH adjusted with NaOH) gave reproducible results for at least one week after preparation.

Partial results of these determinations are shown in Fig. 2 from which it is clear that the most useful concentration is 0.06 *M* with respect to $MoO_4^{-2}$ in reaction, the stock solution being at a pH of about 7.0. With this concentration of ammonium molybdate, complete reaction within two minutes to give the same absorbance value occurs over the pH range of 1.1 to 1.6 (corresponding to the addition of 5.0 to 2.7 equiv. of acid per mole $MoO_4^{-2}$), whilst complete reaction to give a constant absorbance in 10 min occurs in the pH range 0.9 to 1.6 (corresponding to 6.7 to 2.7 equiv. of acid per mole $MoO_4^{-2}$). Variation in concentration of molybdate when considered in relation to pH exerts a considerable effect upon the absolute value of absorbance attained in a given time and, whereas the pH of the stock solution affects the absolute value, its greatest effect is upon the rate of formation of the silicomolybdate complexes.

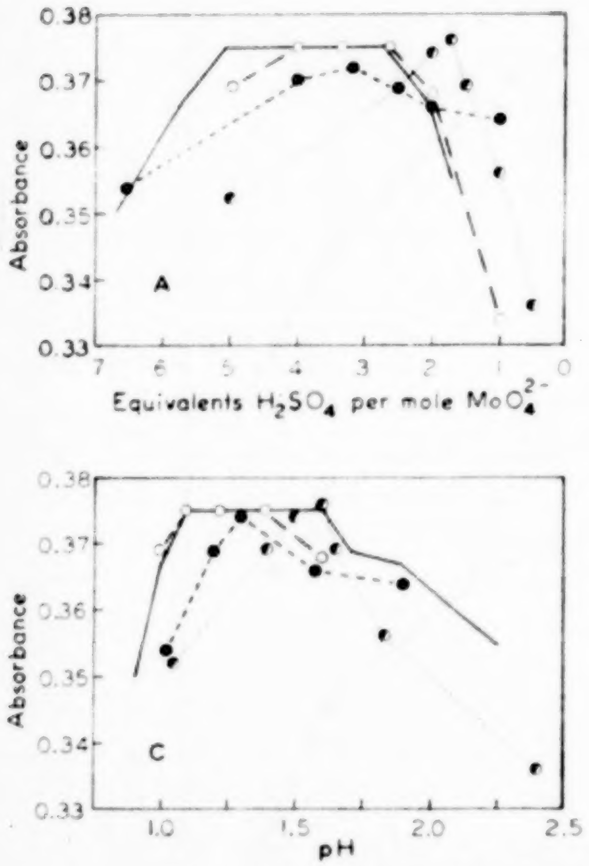

Fig. 2. Comparison of the variation in absorbance of silicomolybdate solutions with acidity and time due to variation in the concentration of molybdate. Sulphuric acid is used to acidify, and the results are shown as a function of both pH and equivalents of acid per mole $MoO_4^{-2}$. ———— 0.06 $M$ with respect to $MoO_4^{-2}$ in reaction. Stock solution 0.3 $M$, pH 7.3; ○ — — ○ 0.06 $M$ with respect to $MoO_4^{-2}$ in reaction. Stock solution 0.3 $M$, pH 6.2; ◐...... ◐ 0.04 $M$ with respect to $MoO_4^{-2}$ in reaction. Stock solution 0.2 $M$, pH 5.2; ● - - - - ● 0.03 $M$ with respect to $MoO_4^{-2}$ in reaction. Stock solution 0.5 $M$, pH 5.2. A, absorbance measured 2 min after start of reaction. B, absorbance measured 10 min after start of reaction. C, absorbance measured 2 min after start of reaction. D, absorbance measured 10 min after start of reaction.

### *Variation in absorbance due to sulphuric and hydrochloric acids*

Two series of experiments over a pH range of 0.5 to 5.5 were run using 1 $N$ $H_2SO_4$ and 1 $N$ HCl respectively. In such series various strengths ammonium molybdate were used, and results for 0.3 $M$ stock solution at pH 7.3 (0.06 $M$ in reaction with respect to $MoO_4^{-2}$) are recorded in Figs. 3 and 4. In Fig. 3, where absorbance is plotted against pH, it is seen that the absorbance at any pH is greater for the HCl series compared with the $H_2SO_4$ series, a difference which becomes more prominent below a pH of 1.0. Although the pattern of the curve for $H_2SO_4$ and HCl is the same, the plateau of high values for HCl is displaced to the acid side compared with $H_2SO_4$.

In Fig. 4 the absorbance is plotted against equiv. of acid per mole $MoO_4^{-2}$. The absorbance after 10 min shows no significant difference between HCl and $H_2SO_4$ until more than 1.5 equiv. acid per mole $MoO_4^{-2}$ have been added; at higher concentrations of acid the absorbance for HCl attains a constant greater value than for corresponding concentrations of $H_2SO_4$. The absorbance values for HCl in the plateau area show a small variation, and are not as consistent as those obtained with $H_2SO_4$.

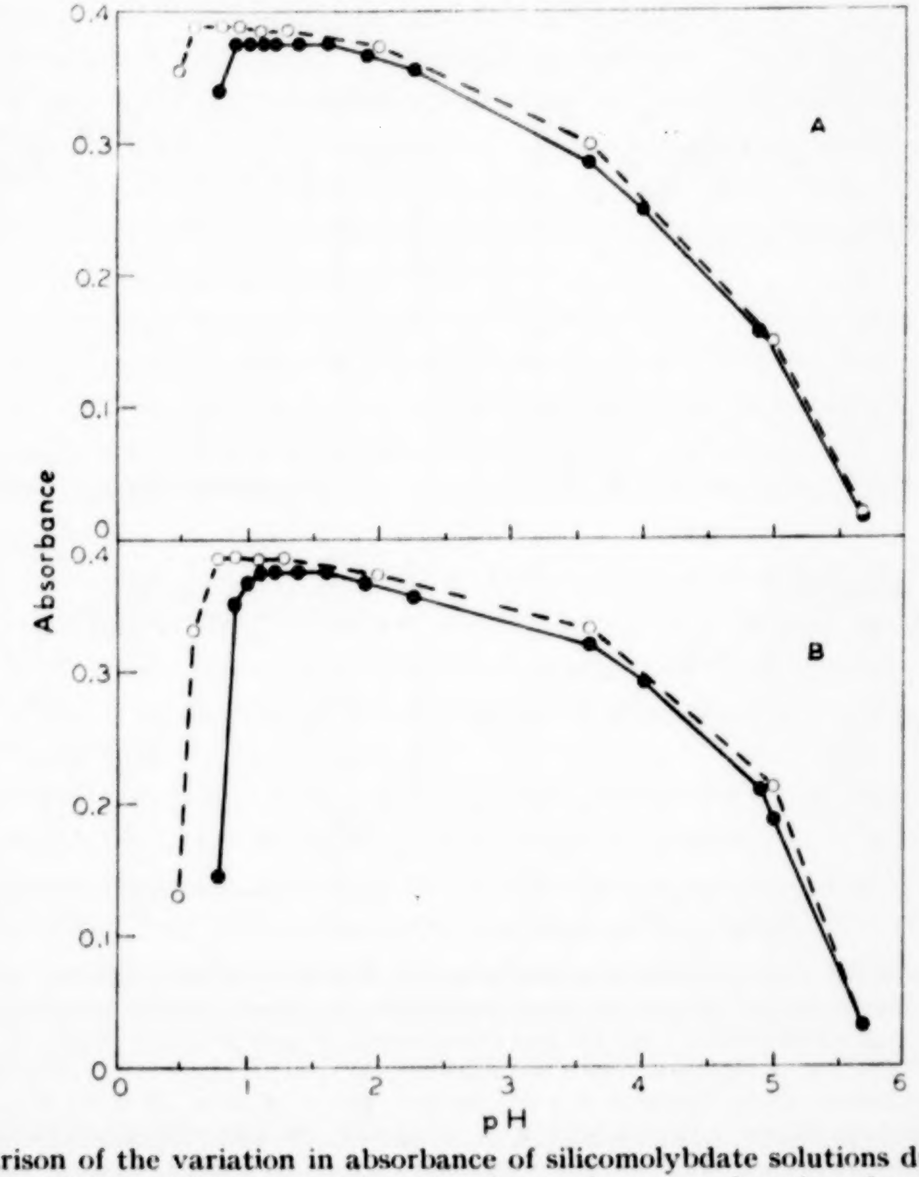

Fig. 3. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of pH. A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction. ●——● acidified with $H_2SO_4$; ○ – – – ○ acidified with HCl.

DISCUSSION

Variation in pH is clearly an important, but not an exclusively responsible, factor in the variation in the development of yellow silicomolybdate complexes. This variation is due to the effect of pH upon the state of the molybdate ions and, as pointed out by MULLIN AND RILEY[13], the rate of formation of silicomolybdate is dependent upon the degree of polymerization of molybdate from which it is formed.

RINGBOM *et al.*[11] quoted LINDQVIST[14] as saying that $MoO_4^{-2}$ ions are stable at pH greater than 6.5, that around pH 4.5 paramolybdate ions ($Mo_7O_{24}^{-6}$) are formed which are transformed into octomolybdate ions ($Mo_8O_{26}^{-4}$) at a pH of 1.5 to 2.9. RINGBOM *et al.*[11] believed that the low-absorbance α-acid is formed from the paramolybdate ion, and the high-absorbance β-acid from the octomolybdate ion. STRICKLAND[10] suggested that concentration must be considered together with acidity: thus, at suitable acidities, and solutions more dilute than 0.01 *M* with respect to $MoO_4^{-2}$,

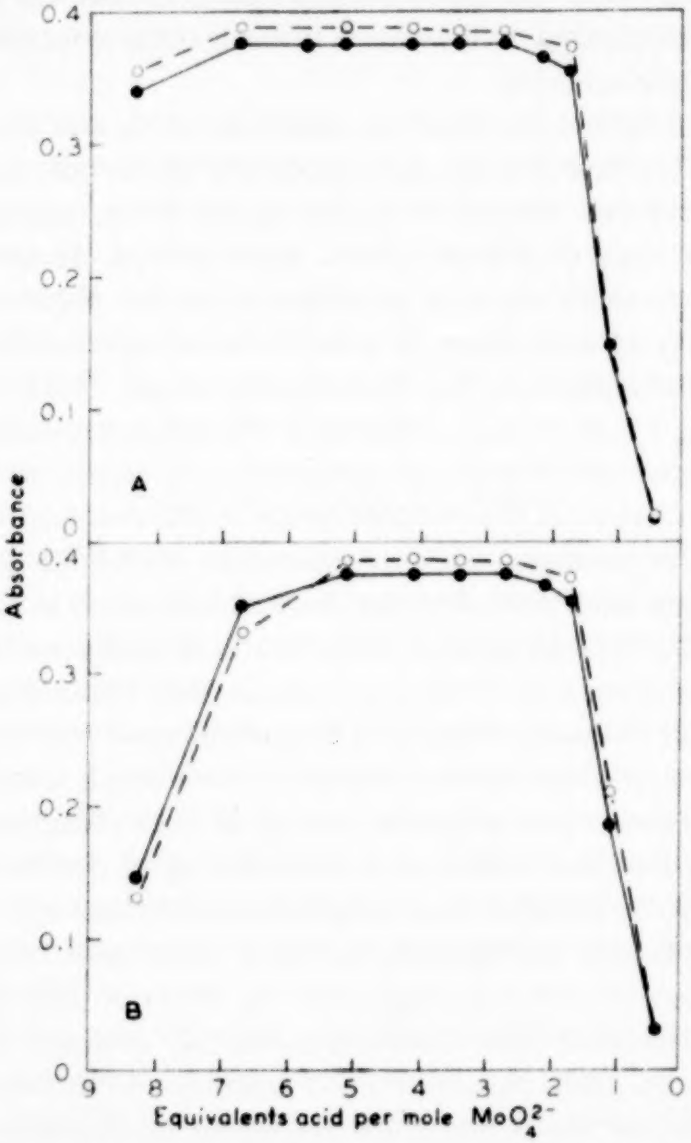

Fig. 4. Comparison of the variation in absorbance of silicomolybdate solutions due to sulphuric and hydrochloric acid as acidifying agencies. Absorbance shown as a function of equivalents acid per mole $MoO_4^{-2}$. A, absorbance measured 10 min after start of reaction. B, absorbance measured 2 min after start of reaction. ○- - -○ $H_2SO_4$; ●——● HCl.

$$4\ MoO_4^{-2} + 6\ H^+ \rightleftharpoons Mo_4O_{13}^{-2} + 3\ H_2O$$

whilst at higher concentrations,

$$5\ MoO_4^{-2} + 4\ Mo_4O_{13}^{-2} \rightleftharpoons 3\ Mo_7O_{24}^{-6}$$

In solutions more concentrated than 0.05–0.1 *M*, and acidified with 1–1.5 equiv. acid,

$$2\ Mo_7O_{24}^{-6} + 4\ Mo_4O_{13}^{-2} \rightleftharpoons 5\ Mo_8O_{26}^{-2}$$

STRICKLAND[10] correlated the β-forming species with the meta ion, $Mo_4O_{13}^{-2}$, but failed to identify the α-forming species. Therefore, the amount of β-silicomolybdic acid formed, and the rate of formation, will depend upon the amount of β-forming species in the molybdate added, and the rate of change of the molybdate at the dilution and acidity in the reaction vessel. This is further complicated by the spontaneous and irreversible change of $\beta$-silicomolybdic acid to $\alpha$-silicomolybdic acid. Thus, if the molybdate is added in such a form and under such conditions that its change to the $\beta$-forming species is very slow, then the earlier-formed $\beta$-acid will have changed to the $\alpha$-acid before all the silica has reacted. This will give low results if the $\beta$-acid is being measured; they will be even lower if some $\alpha$-forming species is initially present in the molybdate added.

Obviously, if the solution chemistry of molybdic acid, and the ion-form of molybdate which reacts with silica to form the various silicomolybdic acids, were completely understood, the molybdate should be added in the form, and into the correct conditions, to yield the form of silicomolybdic acid desired. Inasmuch as solutions of ammonium molybdate made up at a pH of less than 6.5 polymerize with time, and because the chemistry of molybdate in solution is so imperfectly known, it is analytically safer to add molybdate in the form of the simple $MoO_4^{-2}$ ion in solutions of pH greater than 6.5. To allow any latitude in the aliquot of silica solution used the quantity of molybdate added must be comparatively small, and consequently there will be considerable change in the concentration in the reaction vessel compared with the stock solution. For example, adding ammonium molybdate solution at its natural pH of about 5.2 and in such amounts that its concentration in the reaction is 0.03 $M$ with respect to $MoO_4^{-2}$, considerable variation in absorbance was found depending upon whether the solution was diluted to volume (less volume of ammonium molybdate) before addition of molybdate, or all dilution reserved until after addition of molybdate. When using ammonium molybdate from stock solutions at pH 7.3 and in such quantities as to give a concentration of 0.06 $M$ in the reaction, the broad pH zone over which the same constant values are obtained (Fig. 2) results in there being no difference in absorbance due to differences in initial and final acidity in the reaction vessel.

The much reduced rate of reaction between silica and molybdate solutions at acidities greater than pH 1.0 was suggested by MULLIN AND RILEY[13] to be due to polymerization of silicic acid. This is demonstrably not so in solutions less concentrated than about 100 p.p.m. $SiO_2$. An impressive number of workers[1,9,15–17] have shown that monosilicic acid solutions are quite stable up to concentrations of 100 to 150 p.p.m. irrespective of pH. To prove the point, a solution containing 1 mg monosilicic acid at a concentration of about 50 p.p.m. was allowed to stand at a pH of 0.3 for 24 h. This solution was then brought up to a pH of 1.5 and ammonium molybdate added. The absorbance was found to be the same as when the same total reagents were used but the silica added at a pH of 1.5. For these reasons it is believed that STRICKLAND's[10] contention that non-reaction or very slow reaction at high acidities is due to the presence of a non-reactive form of molybdate is correct. STRICKLAND[10] postulated that at very high acidities molybdate is present in a $\gamma$-form, probably as the cationic ion $MoO_2^{+2}$ formed from $\beta$-molybdate. The $\gamma$-molybdate is said to be completely unreactive towards silica, but the slow reaction noted at high acidities is due to a transient stability of the $\beta$-form before its conversion to $\gamma$-molybdate. It may be noted that polymers of silica smaller than 20 m$\mu$ are depolymerized to the monomeric form in the presence of ammonium molybdate[18].

The effect of sulphate ion, as pointed out by STRICKLAND[10] is to cause the development of more $\alpha$-acid (*i.e.* lower absorbance) than a corresponding amount of chloride ion (Figs. 3 and 4). The stability of $\beta$-acid seems to be greater, however, when $H_2SO_4$

is used as the acidifying agent; the maximum color development (in the range 2.7 to 5.0 equiv. acid per mole $MoO_4^{-2}$) is attained within 2 min and remains stable for at least 20 min. Absorbance obtained with HCl shows a slight variation after 2 min in the same acidity range and, unlike $H_2SO_4$, is not exactly the same value over this range. Clearly, although $H_2SO_4$ causes a small reduction in absorbance compared with HCl due to the formation of $\alpha$-acid, the sulphate ion appears to stabilize the $\beta$-acid formed.

Increase in temperature accelerates the change $\beta$- to $\alpha$-acid[10], and boiling temperatures were utilized in the analytical method of RINGBOM *et al.*[11] to ensure the rapid and complete formation of $\alpha$-silicomolybdic acid. There is also a positive temperature-absorbance coefficient for both $\alpha$-acid[11] and $\beta$-acid[10]. A high temperature factor of 0.004 absorbance units per degree centigrade was reported for $\alpha$-acid. The maximum variation found by the writer in admittedly few experiments was 0.001 absorbance units per degree centigrade up to 35°; above 35° the positive variation was offset by the formation of significant amounts of $\alpha$-acid.

## ANALYTICAL CONSIDERATIONS

In formulating a method for the determination of silica, it is desirable that conditions be such that the color is reproducible, stable over a reasonable period of time, relatively insensitive to pH variation, in some cases capable of measuring total and soluble silica, and be as rapid as possible.

It cannot be denied that the observation by RINGBOM *et al.*[11] that the best analytical conditions are obtained by the development of the stable $\alpha$-silicomolybdic acid is most logical. The necessity of boiling the solutions to promote complete formation of the $\alpha$-acid is, however, time-consuming, and leads to complications when it is desired to estimate the amount of monosilicic acid as well as total silica in aqueous samples. Moreover, the sensitivity of the test using the $\alpha$-acid is considerably reduced compared with the $\beta$-acid.

It is believed that the present work completely vindicates STRICKLAND's[10] suggestions that to ensure development of $\beta$-acid it is necessary that the concentration of molybdate be such that $[Mo] = 0.05$ after the silica has combined, and that there should be 3 to 5 gram equiv. of hydrogen ion per gram ion $MoO_4^{-2}$. Whereas most published analytical techniques have strived after the formation of the $\beta$-acid, the lack of concordance between authors and dissatisfaction with the methods (as evidenced by the large number of published works on molybdate methods for determining $SiO_2$) is due to lack of appreciation of the fact that two forms of silicomolybdic acid exist, and insufficient precautions to ensure constant development of one of these forms. Thus, the concentration of ammonium molybdate in the reaction proposed by BUNTING[19] is barely enough to react with 2 mg $SiO_2$ and in no way constitutes an excess as defined by STRICKLAND[10]; the practice of strongly acidifying the ammonium molybdate stock solution allows uncontrolled and unknown polymerization to take place. Methods which advise waiting "about an hour" for the full development of color are clearly open to great variation, whilst heating the sample under conditions of dominant $\beta$-acid formation can only lead to the formation of variable amounts of $\alpha$-acid.

The knowledge that ammonium molybdate reacts rapidly only with monosilicic acid, and the fact that monosilicic acid present in concentrations much above 100 p.p.m.

will polymerize makes the initial treatment of solid samples — and aqueous samples of high silica concentration — of critical importance. It is, therefore, necessary to use weights and volumes such that the concentration of silica in the final sample solution should not be greater than 100 p.p.m. CARRERO AND RAMALLO[20] stated that quartz could be accurately brought into solution at reasonable temperatures and within a reasonable time only with NaOH; the writer has found that $Na_2CO_3$ fusions are liable to give low results, and that solid NaOH should be used for both solid and high-silica aqueous samples.

The interference of other ions has not been investigated during the present study. MULLIN AND RILEY[13] reported upon the interference of a comprehensive list of cations and anions. The most important source of interference likely to be encountered in most geological work is from iron and phosphorous. MULLIN AND RILEY[13] found that by reducing iron with hydroxylamine hydrochloride, 0.2 p.p.m. Si can be determined in the presence of 100 p.p.m. ferric iron with an error of less than 1%; suppression of phosphorous was achieved by addition of oxalic acid after a method by SCHWARTZ[21], allowing 0.2 p.p.m. Si to be determined in the presence of 5 p.p.m. of phosphate with no error. RINGBOM *et al.*[11] recommended the use of EDTA to avoid the formation of precipitates during the dissolution of silicate melts, and although the iron–EDTA complex has a small absorbance at 400 m$\mu$, this can be corrected by a blank; tartaric acid was found to be the best agent to mask phosphorous, but the masking was apparently not complete at 390 m$\mu$. LINDSAY AND BIELENBERG[22] used sodium citrate to destroy the phosphomolybdate complex, whilst BUNTING[19] employed tartaric acid for the dual purpose of suppressing both iron and phosphorous.

The employment of the reduced blue silicomolybdate complex offers a number of analytical advantages — there is no temperature coefficient and it has greater sensitivity — but suffers the disadvantage of being time-consuming and not well suited if it is desired to estimate the proportion of monosilicic acid as well as total silica in aqueous samples. The success or failure of the reduction method depends upon the same factors as when employing the unreduced complex, although the reducing agent may be of importance in some cases[13]. As determined by STRICKLAND[10], formation of a mixture of $\alpha$- and $\beta$-silicomolybdic acids either initially or by rapid change of $\beta$- to $\alpha$-acid, will give on reduction a mixture of $\alpha$-silicomolybdous (greenish-blue) and $\beta$-silicomolybdous (royal blue) acid which have markedly different absorbance at wavelengths used, *i.e.* above 625 m$\mu$.

### *Method adopted*

*Preparation of sample.* Solid samples should be fused with solid NaOH (in the ratio of about 3 g NaOH to 0.1 g sample) in nickel crucibles for at least 10 min. The melt is leached into a plastic beaker and acidified with sufficient 1 *N* sulphuric acid to give a pH of about 1.5 to the final solution. The total dilution will depend upon the amount of silica anticipated in the sample; the dilution may be achieved by diluting to volume in 500- or 1,000-ml volumetric flasks or, for greater accuracy, by diluting by weight in the plastic beaker. It must be stressed that the sample solution must not be strongly alkaline when added to glassware, for silica will be dissolved leading to erroneous results.

When it is desired to determine total silica in aqueous samples, a suitable aliquot should be boiled with solid NaOH in a nickel beaker, and then diluted as above. No treatment is necessary for determination of soluble silica.

*Procedure.* A suitable aliquot of sample solution is added to a 50-ml volumetric flask, acidified with 10 ml 1 *N* $H_2SO_4$, and followed by 10 ml of 0.3 *M* (with respect to $MoO_4^{-2}$) ammonium molybdate. The latter solution is prepared by dissolving 52.97 g of crystalline $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ in one litre of water with sufficient sodium hydroxide to give a pH of not less than 7.0. The sample is diluted to 50 ml with distilled water. The absorbance is measured at 400 m$\mu$ (at a slit width of 0.04 m$\mu$ when using a Beckman Model DU spectrophotometer). The reaction with monosilicic acid is complete within 2 min and if the proportion of monosilicic acid is to be determined in an aqueous sample, the reading should be taken at 2 min; if total silica is being determined (which, of course, will be present as monosilicic acid after sample treatment) the reading should be taken not sooner than 2 min nor later than 10 min after addition of ammonium molybdate.

Calculation of the silica content is made by reference to a standard curve. Standard silica solutions may be prepared either directly by dissolving sodium metasilicate ($Na_2SiO_3\cdot 9\,H_2O$) in distilled water acidified with $H_2SO_4$ so that the final pH is about 1.5 (about 60 ml 1 *N* $H_2SO_4$ per litre) or by fusion of standard felspar or pure quartz in the same manner as outlined for preparing solid samples for silica determinations. The concentration of the stock solution should not be greater than 100 p.p.m. $SiO_2$; 50 p.p.m. $SiO_2$ was found to be suitable. Aliquots of the standard solution are used to prepare a standard curve for concentrations up to about 2 mg $SiO_2$ per 50 ml. It is important that the standard determinations should be made with the same reagents present in the same amounts as the unknown samples.

*Treatment of glassware.* Dirty glassware should be thoroughly cleaned with chromic acid cleaning solution, followed by washing, and then a further cleaning with 1 : 1 HCl, and a final wash with distilled water. If the glassware is regularly cleaned, it is sufficient to wash with 1 : 1 HCl. The writer confirmed the observation by Mullin and Riley[13] that if glassware is allowed to dry, even after the most stringent washing, it has an appreciable solubility under the conditions of the test. It was found convenient to leave the 50-ml volumetric flasks standing in an acid-bath containing 1 : 1 HCl, and wash well with distilled water just before use.

Replicate determinations with a standard silica solution showed a maximum standard deviation of 0.002 absorbance units in the range 0.1 to 1.0 mg silica per 50 ml. Maximum deviation occurred in the range 0.1 to 0.2 and again in the range 0.7 to 1.0 mg $SiO_2$ per 50 ml. The higher deviation in the lower range is attributed to pipetting error, whilst in the higher range it is probably due to lack of instrument-reading sensitivity. These determinations were carried out by the method outlined above with no special temperature control, and the standard deviation found does not include errors due to weighing or diluting of the sample; nevertheless, it is believed that it represents an adequate degree of accuracy.

## ACKNOWLEDGEMENTS

This paper results from an investigation of the dissolution of silicate minerals in aqueous solution being conducted in co-operation with Dr. C. P. Gravenor, whose comments and advice are appreciated. Thanks are extended to Dr. T. Rigg (Research Council of Alberta) and Drs. D. A. W. Sharp and N. A. Gill (Department of Chemistry, Imperial College, London, U.K.) for their helpful advice on the manuscript.

## SUMMARY

The development of rapid colorimetric analytical techniques for silicates has catalysed many fundamental research programs in the geological sciences. Despite a multitude of papers on the silicomolybdate colorimetric technique for the analysis of silica which appear in the journals of nearly all sciences, it was found extremely difficult to adapt any published method for a particular purpose, and obtain reliable results. This is due to a lack of appreciation of the factors which control the silicomolybdate reaction. Data are given which indicate that the major factors are the polymer species of molybdate, which is controlled largely by the pH of molybdate stock solution; the concentration of molybdate; the ratio of acid to molybdate in reaction; and the type of acid used in the reaction. The effect of these variables is outlined, and an analytical procedure for both "soluble" and total silica outlined.

## RÉSUMÉ

Une étude critique a été effectuée au sujet du dosage colorimétrique de la silice sous forme de silicomolybdate. Divers facteurs ont été examinés et la méthode, finalement adoptée, pour le dosage de la silice "soluble" et de la silice totale est décrite.

## ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die colorimetrische Bestimmung von Kieselsäure als Silikomolybdat. Unter Berücksichtigung des Einflusses der verschiedenen Faktoren (pH, Konzentration etc.) wird ein Verfahren zur Bestimmung von löslicher und Gesamtkieselsäure angegeben.

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# THE SPECTROPHOTOMETRIC DETERMINATION OF STRONTIUM WITH MUREXIDE (AMMONIUM PURPURATE)*

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(Received November 17th, 1960)

There have been comparatively few procedures recommended for the spectrophotometric determination of strontium. Of three that have been developed, that involving chloranilic acid as the reagent[1] is an indirect method of low sensitivity. The others, both produced by POLLARD AND MARTIN[2], use murexide and *o*-cresolphthalein complexone respectively as the reagents. Unfortunately, the experimental results upon which these two methods are based were not recorded by the authors.

Attempts in this laboratory to utilize the murexide procedure in order to determine $\mu$g-quantities of strontium were unsuccessful. This was apparently due to the instability of both the murexide reagent solution and the strontium-murexide complex produced when the recommended procedure was followed. As a result we have made a further study of the spectrophotometric determination of strontium with murexide and this communication describes a modified method which we have found useful for determining small amounts of strontium.

Murexide is a highly coloured substance which forms chelates with many metal ions. These metal chelates differ in colour with the strength of binding and the pH of the solution. The material has found wide use as a metal indicator in complexometric titrations, especially for the EDTA titration of calcium. It has been used by several workers for the photometric determination of macro quantities of this metal in neutral solution[3,4], and $\mu$g amounts in alkaline medium[5,6]. The latter procedure[6] employing a solution of the dye in 70% (v/v) ethanol was adapted for the determination of strontium by POLLARD AND MARTIN[2] by increasing the reagent concentration and taking precautions to minimize the differential errors between the blank and sample solutions due to the high rate of decomposition of the murexide reagent.

We have found that a solution of murexide in 80% (v/v) ethylene glycol results in a reagent of greatly enhanced stability, and addition of ethylene glycol to the reaction mixture results in a stable strontium-murexide complex.

## EXPERIMENTAL

Photometric measurements were made with a Beckman Model DU spectrophotometer and optically matched 1.00-cm cells. A constant slit width of 1.0 mm was used since the reagent blank was quite optically dense and small variations in slit at the wavelength employed (510 m$\mu$) resulted in substantial variations in absorbance. Spectral curves of the coloured solutions were made with a Beckman Model DK-1 recording spectrophotometer.

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* N.R.C. publication No. 6279.

*Anal. Chim. Acta*, 25 (1961) 81-84

Murexide was obtained from two sources: J. T. Baker Chemical Co. ("Baker Analyzed" Reagent) and Siegfried Chemicals and Pharmaceuticals, Switzerland. All chemicals used were of analytical reagent or C.P. grade. One batch of ethylene glycol was found to be contaminated with a small amount of calcium and was redistilled before use.

### *Development of the procedure*

Initially, attempts were made to stabilize the reagent solution and the colour system by varying some of the conditions recommended by POLLARD AND MARTIN[2]. These included (*i*) varying the percentage of ethanol in the reagent, (*ii*) adding ethanol in various proportions to the reaction mixture, (*iii*) varying the pH slightly by the addition of more or less 0.05 *M* sodium hydroxide solution, (*iv*) varying the reagent concentration and (*v*) keeping the reagent and samples at 0° in an ice-water bath before mixing and cooling the cell compartment of the spectrophotometer to less than 20° by passing cold water through a pair of thermospacers bracketting the compartment. These were all unsuccessful, although enhanced stability was obtained with the cold solutions.

BRUNISHOLZ *et al.*[7] had reported that a saturated solution of murexide in anhydrous ethylene glycol provided a fairly stable dye solution for use as a metal indicator. A solution of this type was prepared and found to be very stable when kept refrigerated. However, it was found difficult to reproduce these solutions as the murexide concentration varied widely from batch to batch. Solutions of murexide in 80% (v/v) ethylene glycol were found to be of equal stability, and could be easily prepared at a given concentration. A 0.05%-solution of the dye in this medium was chosen as the reagent. One batch of this reagent was used over a period of six weeks with no apparent deterioration.

In experiments to find optimum conditions for the colour reaction the following basic procedure was followed. A solution containing 93.8 μg of strontium as the chloride was transferred to a 25-ml volumetric flask, and ethylene glycol and 0.05 *M* sodium hydroxide were added. The solution was well mixed and set in an ice-water

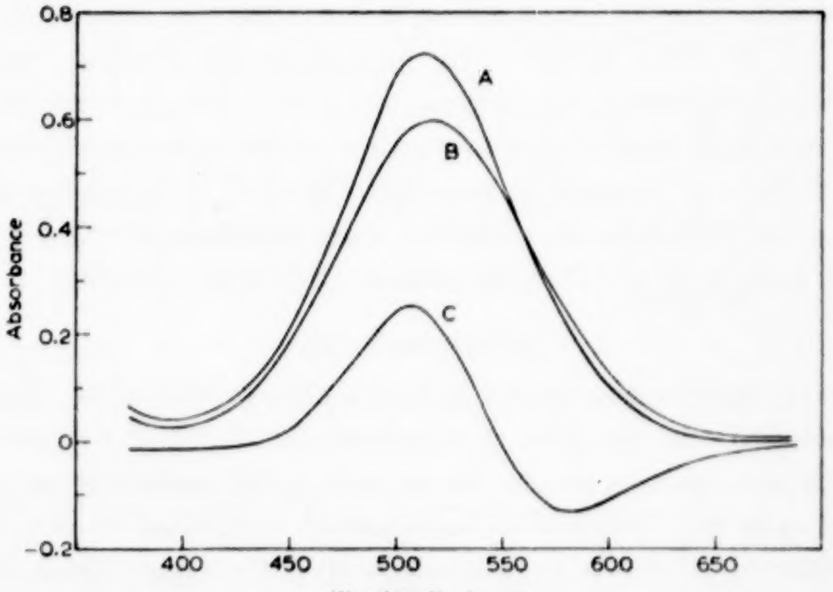

Fig. 1. Typical spectra of murexide and the strontium complex. A, reagent blank against water. B, reagent plus strontium against water. C, reagent plus strontium against a reagent blank.

bath to cool. After cooling, the cold reagent was added, the solution was made up to volume with water, shaken, and the absorbance measured against a reagent blank which was simultaneously prepared.

The preparation of simultaneous blanks is essential. Although the murexide reagent is quite stable when refrigerated, it decomposes slowly at room temperature. Any differential errors due to this decomposition are minimized by this precaution. The rate of reagent deterioration can be reduced appreciably by cooling the cell compartment, but this was not deemed necessary.

Typical spectra of the reagent and strontium–murexide complex are shown in Fig. 1. Since the absorbance of the reagent is relatively high, curves A and B which represent absorbance curves of the reagent blank and of a sample respectively measured against water, have been reduced in size so that a better comparison can be made with curve C which represents a sample measured against a reagent blank. The absorbance maximum of curve C was found to be at 510 m$\mu$.

The stability of the coloured complex was directly proportional to the quantity of ethylene glycol added to the system (Fig. 2). 15 ml was chosen for all subsequent determinations.

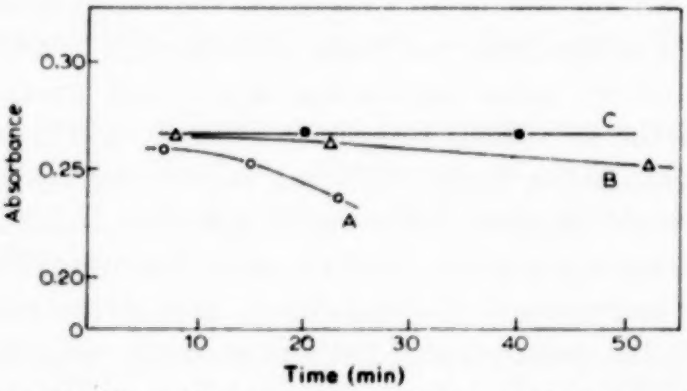

Fig. 2. Effect of ethylene glycol on the stability of the strontium complex. A, 5.0 ml ethylene glycol added. B, 10.0 ml ethylene glycol added. C, 15.0 ml ethylene glycol added.

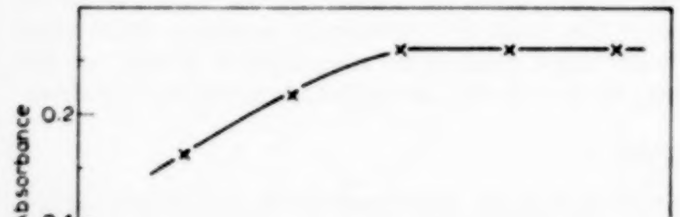

Fig. 3. Effect of varying amounts of reagent.

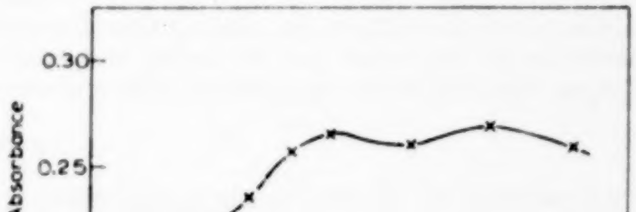

Fig. 4. Effect of varying amounts of sodium hydroxide solution.

The absorbance increased with the quantity of reagent added until a maximum was reached at 3.0 ml (Fig. 3).

Also, with 3.0 ml of reagent, the absorbance increased with the quantity of 0.05 *M* sodium hydroxide added, levelling off at about 3.0 ml (Fig. 4). Although a slight increase in sensitivity may have been obtained at 5.0 ml, 3.0 ml was chosen as the optimum amount in order to keep the pH as low as possible, enhancing the stability of the coloured species. The pH of this solution was found to be 11.3.

Beer's law is followed up to approximately 8 $\mu$g per ml, after which the slope of the absorbance curve steadily decreases with increasing strontium concentration. Increasing the quantity of reagent had no effect on this curve.

Six replicate samples, each containing 93.8 $\mu$g of strontium in a final volume of 25 ml gave a mean absorbance of 0.265 with an average deviation of 0.003 or 1.1%.

Experiments showed that most elements usually associated with strontium interfere in this determination, even when present in very small amounts. For example, the following quantities in $\mu$g produce an approximately 5% increase in the absorbance due to 93.8 $\mu$g of strontium; Mg: 300, Ca: 2, Ba: 50, Li: 75, K: 150, Ag: 10.

These interferences can generally be removed by ion exchange[8,9] or paper chromatography[10]. In our own case where we were interested in the analysis of small quantities of silver-strontium alloys used in X-ray diffraction work a micro precipitation of silver as silver chloride served to reduce the silver concentration to below the level of interference.

### *Recommended procedure*

*Reagent:* Prepare the 0.05%-murexide reagent by dissolving 125 mg of the dye in 50 ml of water and adding 200 ml of anhydrous ethylene glycol. Allow the solution to stand overnight in a refrigerator and filter cold through a Whatman No. 42 paper. Keep the solution in an ice-water bath when in use and store under refrigeration.

*Method.* Evaporate the strontium sample to dryness and transfer with a few ml of water to a 25-ml volumetric flask. Add 15.0 ml of ethylene glycol and 3.0 ml of 0.05 *M* sodium hydroxide solution. Dilute with water to about 22 ml. Mix well and cool the solution in an ice-water bath. Add 3.0 ml of the murexide reagent and dilute to volume. Shake well and measure the absorbance in matched cells at 510 m$\mu$ against a reagent blank which has been prepared simultaneously with the sample.

## SUMMARY

A procedure for the spectrophotometric estimation of $\mu$g-quantities of strontium with murexide is described. Conditions for the optimum stability of the coloured strontium complex have been determined, the main feature being the addition of large quantities of ethylene glycol to the system. Most elements interfere so that it is necessary to isolate the metal before the determination.

## RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du strontium au moyen de murexide. De nombreux éléments gênant, une séparation préalable est nécessaire.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmung von Strontium mit Murexid. Wegen des störenden Einflusses der meisten anderen Elemente ist eine Abtrennung erforderlich.

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# SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS

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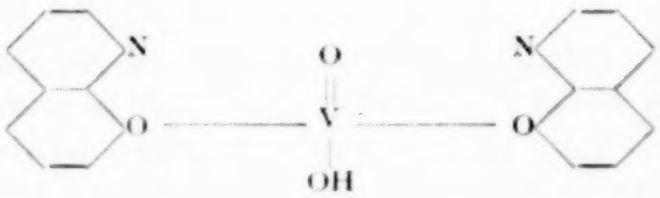
(Received November 26th, 1960)

## INTRODUCTION

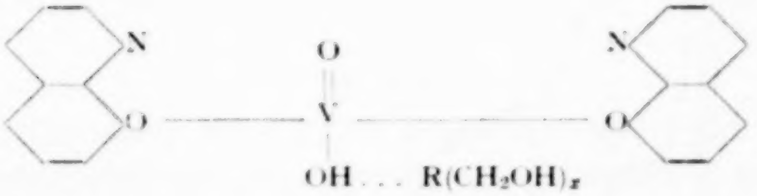
When organic solvents are used in extraction processes, it is often necessary to determine small amounts of esters or alcohols in the organic or aqueous phases.

Feigl[1,2] mentions a spot test for alcohol as follows: vanadium(V) forms a complex with oxine[3,4] in an acetate medium, the ratio of vanadium to oxine being 1 : 2. The complex is insoluble in water and acetic acid but dissolves in benzene, chloroform, acetone, alcohol and trichlorethylene, giving a dark greyish-green colour to the organic phase.

If alcohol is added to the suspension of the vanadium complex in water and an extraction with benzene is carried out, the organic layer appears red. It is presumed that a second complex with the alcohol is formed (II) which is more stable than the initial vanadium oxine complex (I).



I



II

This secondary complex (II) is formed with primary, secondary and tertiary alcohols but not with alcohols containing a phenolic or carboxylic group (citric or lactic acid, phenol) except where the carboxylic group has undergone esterification *e.g.*, the ester of lactic acid.

Buscarons, Marin and Claver[5] examined the colours obtained by dissolving vanadium oxinate in a long series of organic compounds. They found that the reddish colour is given only with alcohols. These authors report a sensitivity limit of 1.5%–2.5% alcohol in a mixture of organic solvents and 2.5%–5% alcohol, when testing an aqueous solution.

If the aqueous phase (pH 3.5–5) contains insufficient alcohol together with the precipitate of vanadium oxinate, two colours are observed on extraction in the benzene layer:

*1.* the reddish colour of the alcoholic vanadium-oxinate complex.

*2.* the grey-black colour of the excess vanadium oxinate.

If it were possible to eliminate the vanadium-oxinate complex (I) from the organic phase leaving only the complex (II), a quantitative determination of small amounts of alcohol would be feasible. Such a method is described here.

When the organic coloured layers are washed with *N* sodium hydroxide solution, the vanadium oxinate is transferred to the aqueous phase, while the alcohol complex remains in the organic phase along with part of the excess oxine.

## EXPERIMENTAL

### *Absorption as function of wavelength*

Determination of the absorption of the alcohol complex in benzene solution at various wavelengths was carried out at a concentration of 1.8 mmole of alcohol; methyl, ethyl, butyl and amyl alcohols were tested (see Fig. 1). In these experiments only one benzene extraction was done. Similar curves were obtained for the four alcohols. The highest absorption was obtained with amyl alcohol; absorption decreased through butyl and ethyl to methyl alcohol. In all four spectra two flat areas (plateaux) were found in the two regions, 370–400 m$\mu$ and 450–480 m$\mu$.

In Fig. 1, it is difficult to see the flattened areas of the methyl alcohol complex

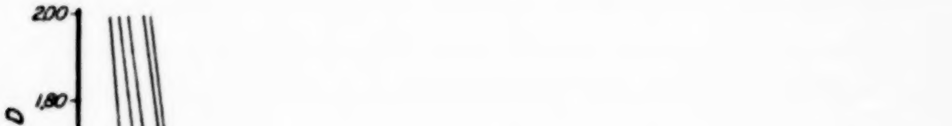


Fig. 1. Absorption of alcoholic vanadium-oxinate complexes as function of wave-length (Beckmann DU spectrophotometer). ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex; ϕ without alcohol.

but when the above experiment was repeated with large quantities of methyl alcohol the curve was the same as for the other alcohols.

A control containing all the reagents used, but no alcohol, was also examined.

The spectrum of the control is apparently given by oxine (which is present in excess) and which remains partly soluble in benzene even after the extraction of the vanadium oxinate with alkali from the organic phase. The spectrum found for the control has the same features as that found by MOELLER[6] for oxine (see $\phi$ in Fig. 1). It can be seen that the first flat area of the spectrum is an area of maximum absorption for the vanadium-oxinate-alcoholate complex. For quantitative determinations therefore, a wavelength of 390 mμ was chosen. At this wavelength, sensitivity is highest and the influence of oxine on the readings very small.

### *Reagents*

(*1*) Solution of ammonium vanadate containing 1 mg of vanadium per ml.
(*2*) 2.5% solution of 8-hydroxy-quinoline in 6% acetic acid.
(*3*) Buffer solution of acetic acid-sodium acetate, pH = 4 (100 ml of acetic acid and 53.5 g of sodium acetate).
(*4*) Benzene, Baker analytical reagent.

The two phases were kept at fixed relative volumes, the ratio of the organic to aqueous phase being 2 : 1.

### *Procedure*

1 ml of ammonium vanadate solution and 1 ml of the oxine solution were added to the sample under test (containing 50-500 μg of alcohol) followed by buffer solution to a volume of 7 ml.

The mixture was shaken in a Burrell wrist action shaker with 15 ml benzene for 20 min. After separation of the phases, extraction from the aqueous phase was repeated twice with fresh quantities of benzene and the other reagents.

The benzene extracts were collected and, after washing with 10 ml of *N* sodium hydroxide solution, the optical density was read in the spectrophotometer; a Coleman universal spectrophotometer or a Beckman DU quartz spectrophotometer was used.

## RESULTS

Fig. 2 shows the relationship between the concentrations of four different alcohols in the benzene solution and the optical density of the complex at 390 mμ after correction for the blank. As might be surmised from Fig. 1, the sensitivity increases with the molecular weight. The maximum deviation in results is ± 2.5%. The relative mean deviation is usually 2%. The smallest quantities of alcohol which could be detected are shown in Table I.

TABLE I

| | *Concentration in the final benzene solution, μg/ml* | *Concentration in the original sample, μg/ml* |
|---|---|---|
| Butyl or amyl alcohol | 1 | 10 |
| Ethyl or methyl alcohol | 2-3 | 20-30 |

The proportionality of optical density to concentration was checked up to a concentration of 16–20 μg of alcohol per ml of the final benzene solution (see Fig. 2).

From Fig. 2 it also appears that the sensitivity of the amyl alcohol complex is less than that of the butyl alcohol. If the amounts of alcohol are calculated in mmoles

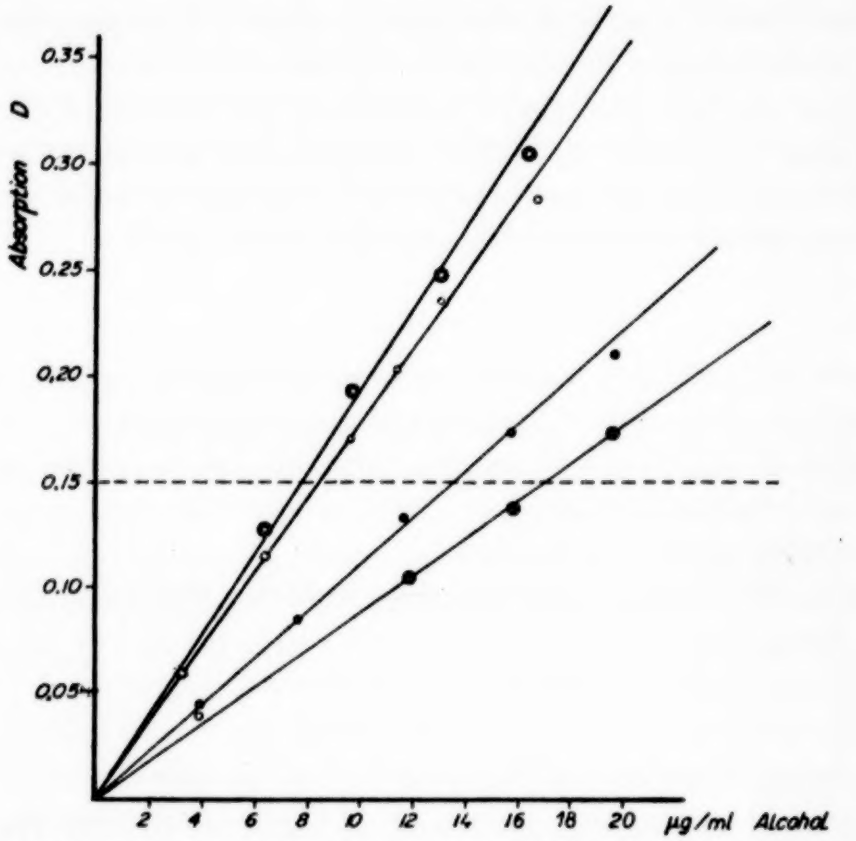


Fig. 2. Absorption as function of alcohol concentration (weight units), $\lambda = 390$ mμ. Coleman Senior spectrophotometer. ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex.

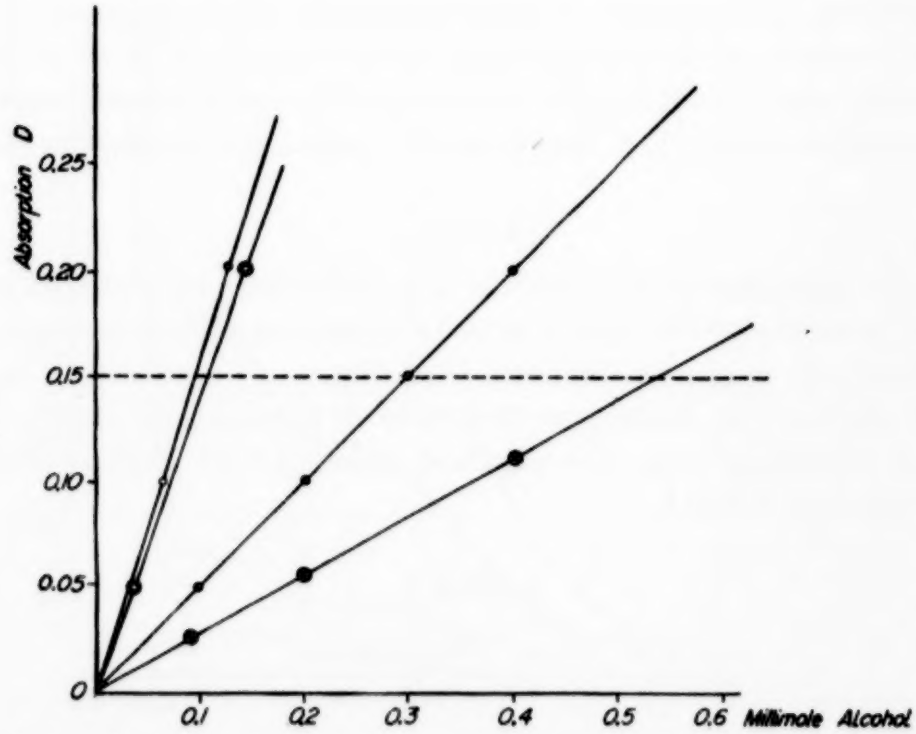


Fig. 3. Absorption as function of alcohol concentration in molar units ($\lambda = 390$ mμ). Coleman Senior spectrophotometer. ○ amyl alcohol complex; ◎ butyl alcohol complex; ● ethyl alcohol complex; ◉ methyl alcohol complex.

at the same optical density of 0.15, for example, the curve for the amyl complex appears higher than that for the butyl complex.

This is clearly seen in Fig. 3 where curves are given of optical density as a function of molar concentration of alcohol.

In Table II, some physical constants of the alcohols are given.

Possible cation interferences have not been studied but data collected from the literature[6-8] shows that the metals extracted with oxine at pH 4–5 are: Al, Bi, Cu, Fe, In, Mo, Ni, Ru(III), Pu(IV, VI), Sn(IV), Ti, V, W, Zn. Of these metals, only copper is totally extracted at pH 14, while no aluminium or iron and probably no molybdenum, nickel, titanium or vanadium is extracted.

TABLE II

PHYSICAL CONSTANTS OF ALCOHOLS

| *Alcohol* | | *Mol. wt.* | *Dielectric constant of the alcohol* | *Molecular extinction coefficient of vanadium-oxinate complex (according to Beer's law)* |
|---|---|---|---|---|
| Methyl | ($CH_3OH$) | 32 | 32.6 | 175 |
| Ethyl | ($C_2H_5OH$) | 46 | 24.3 | 312 |
| Butyl | ($C_4H_9OH$) | 74 | 17.1 | 890 |
| Amyl | ($C_5H_{11}OH$) | 88 | 13.9 | 1000 |

## ACKNOWLEDGEMENT

The author wishes to thank Dr. J. Yofe, Head of the department, for advice and assistance in this work.

## SUMMARY

A spectrophotometric method for the determination of small amounts of methyl, ethyl, butyl and amyl alcohols is described. The sensitivity of the method is of the order of 10 $\mu$g/ml of test solution in the case of butyl and amyl alcohols and 20–30 $\mu$g/ml in the case of ethyl and methyl alcohols. The molar extinction coefficient rises with the molecular weight of the alcohol. The nature of the alcoholic complex is not yet known.

## RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage des alcools méthylique, éthylique, butylique et amylique. On observe que le coefficient d'extinction moléculaire augmente avec le poids moléculaire de l'alcool.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung kleiner Mengen Methyl-, Aethyl-, Butyl- und Amylalkohol mit Hilfe des Vanadiumoxinat Komplexes. Es wurde festgestellt, dass der molekulare Extinktionskoeffizient mit zunehmenden Molekulargewicht des Alkohols grösser wird.

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# SPECTROGRAPHIC DETERMINATION OF BORON IN NUCLEAR GRAPHITE

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(Received December 21st, 1960)

The use of graphite as a power reactor moderator necessitates a study of analytical methods for the determination of very low concentrations of those elements which show a high neutron cross section. Amongst these elements is boron, which is usually present in graphite and for which normal purification processes are ineffective. The chemical determination of boron at the concentrations which do not affect the reactor performance requires difficult and time-consuming techniques.

The purpose of this work was to develop a method for the spectrographic determination of the boron content of nuclear graphite at concentrations between 0.1 and 1.0 p.p.m. Such a method had to be, moreover, rapid and economical, *i.e.* properly developed for low-cost routine analysis on thousands of samples.

It was deemed advisable, due to cost problems, to eliminate the use of boron-free graphite for the electrodes. For this reason, among the methods in the literature we excluded the possibility of adapting the methods of FELDMAN AND ELLENBURG[1], RÜSSMANN[2], SHUGAR[3], GARTON[4] or LEPPLA AND MARKEL[5]. Some of these methods were also excluded because the sensitivity indicated by their authors did not meet our requirements.

The addition of substances as internal standards and their accurate mixture — as far as graphite is concerned — are rather tedious operations (as RÜSSMANN[2] points out). Therefore the possibility was studied of using the background as an internal standard with considerable time saving in the preparation of analysis samples. The selection of background as internal standard proved to be quite satisfactory and effectively allowed the use of the sample itself without any handling other than shaping.

## APPARATUS

A "Hilger" medium quartz spectrograph (type E 498; dispersion at 2500 Å approx. 9 Å/mm) was employed for the determinations. For a rapid consumption of the sample, an arc source of 380 V d.c. and delivering a 20-A maximum output, was constructed. For the direct sample support, metallic (brass) electrode holders were adopted. Ilford ordinary plates were used and were developed by Ilford ID2.

## EXPERIMENTAL

For the preliminary work we considered the possibility of analysing both block and powder samples. Of course it is easy to obtain cylindrical sticks from blocks for the formation of the two electrodes. On the other hand, powder samples require working up and moulding.

For this purpose we adapted the method used by GARTON[4] to prepare graphite pellets suitable for insertion on the end of his boron-free graphite electrodes.

The method was as follows: to 5 parts of finely powdered sample (approximately 100 mesh), one part of bakelite solution was added (we used the SUPERBOL product of Monti & Martini Co. which blank tests showed to be boron-free). The substances were mixed thoroughly and accurately and the mixture was dried at 110°. The sample was subjected at 150° to a pressure of 14,000 p.s.i. Rectangular rods which were 5 mm wide and 20-25 mm high were obtained. Such electrodes were used with a 17-A arc. In order to obtain sufficiently intense boron lines, a rather high sample consumption and relevant exposure time were required. On the other hand it was necessary to prevent the background from reaching prohibitive values; for this purpose the spectrograph was illuminated by an intermediate image of the arc from which the electrode image was removed by masking. The electrode spacing was maintained during exposure at 4 mm and the slit width was 5 $\mu$.

Before exposure, electrodes were arced for a few seconds in order to eliminate any traces of volatile and easily inflammable bakelite residues. The arc was then re-lighted for 3 min for the exposure. Electrode masking allowed such a long exposure time without excessive background values around the two boron lines. Plate calibration was made by the two-step filter method on an iron spectrum.

As the boron analytical line, we used BI 2497.73, on which no interference has been noted by the elements present as impurities in nuclear graphite. As background value the minimum blackening value between B 2496.78 and B 2497.73 lines was employed.

## RESULTS

The calibration curve was plotted by starting with two analyzed powdered graphite samples containing 1.05 and 0.10 p.p.m. of boron respectively. By mixing the first with Ringsdorff RWD graphite powder (boron-free), two other samples were obtained containing 0.525 and 0.210 p.p.m. of boron. Once the electrodes had been obtained and arced as described above, the calibration curve was determined (Fig. 1). The abscissa values indicate the boron concentration in the initial sample, *i.e.* before bakelite mixing.

Boron lines proved to be easily measurable for concentrations ranging from 0.2 to 1.0 p.p.m.; between 0.1 and 0.2 p.p.m., insufficient blackening against the background allows only a semiquantitative estimation.

The points shown on the calibration curve are the average of three relatively consistent values.

When a series of electrode couples containing 0.525 p.p.m. of boron were arced twelve times in the same plate, the reproducibility of the method proved to be $\sigma\% = 9.8$, which was quite suitable for our purposes, especially if the data are used as the average of 3 or 4 determinations.

Different values for samples of the same concentration, were found only when the results were obtained with electrodes which were considerably different in geometric size from couple to couple, or when the same couple was used for more than one exposure.

For samples directly cut from blocks of the same boron content, the line-to-background ratio was found to depend on material aggregation and other uncontrollable factors. For this reason, the direct arcing of solid samples (cut from blocks) was impracticable because it would have been necessary to prepare as many calibration curves as the types of graphite to be tested.

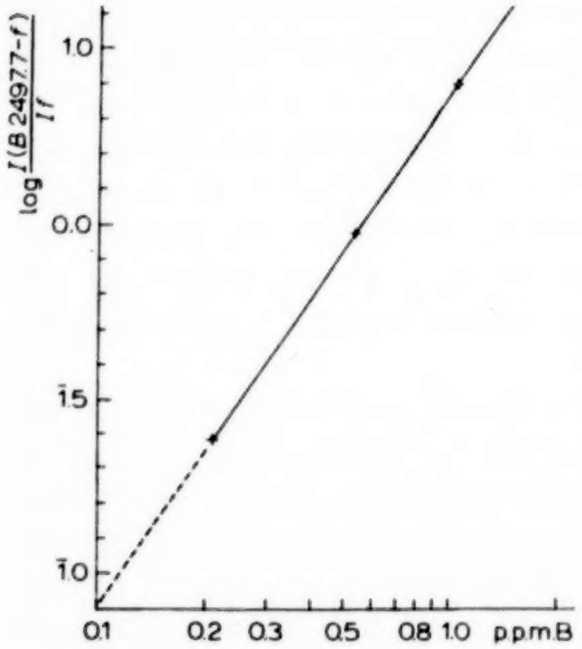

Fig. 1. Calibration curve for boron in graphite.

## CONCLUSIONS

The method described is of practical and economic value for the analysis of a large number of powdered or pulverizable samples. The precision of the method is sufficient for the concentration range under consideration. The time required for analysis of at least 10 samples, each being analyzed three times and the calibration curves being replotted on each plate, is approximately 1 sample/2 h/worker; this includes all operation times from preparing the samples to the final calculation. The method is therefore suitable for graphite stock analysis for nuclear reactor purposes.

A much more detailed account of this work will be published in Italian in *Metallurgia Italiana*.

## SUMMARY

A spectrographic method is described for the determination of boron (0.2–1.0 p.p.m.) in nuclear graphite and for the estimation of 0.1–0.2 p.p.m. of boron. Neither boron-free graphite electrodes nor additional foreign substances as internal standard are required. Both the electrodes consist of sample powder, properly bakelite-processed. The standard deviation is 10%.

## RÉSUMÉ

Une méthode spectrographique est décrite pour le dosage du bore dans le graphite destiné à l'usage nucléaire, pour des teneurs de 0.2 à 1.0 p.p.m. Les deux électrodes sont constituées par la poudre de l'échantillon à analyser comprimée et durcie par "bakélisation".

## ZUSAMMENFASSUNG

Beschreibung einer spektrographischen Methode zur Bestimmung von sehr kleinen Mengen Bor in Kernreaktionen-Graphit, wobei die Elektroden aus dem zu untersuchenden Graphit mit Bakelit als Kittsubstanz bestehen.

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# PILOT-ION COULOMETRY WITH DROPPING MERCURY ELECTRODES

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(Received December 5th, 1960)

## INTRODUCTION

Coulometric measurements with dropping mercury electrodes have been employed to determine polarographic $n$-values in three different ways.

One[1-3] involves the periodic measurement of the diffusion current of the substance in question during a prolonged electrolysis of a known volume of solution with a dropping electrode, and the calculation of $n$ from the slope of a plot of log $i_d$ *versus* electrolysis time. In another[2], the number of coulombs flowing during such an electrolysis is measured and compared with the change of diffusion current that occurs: if the amount of material originally present is known, and if the fraction of it that is reduced is calculated from the ratio of diffusion currents before and after the electrolysis, $n$ can be obtained from Faraday's law. In the third[4], the electrolysis current is passed through a second dropping electrode in a solution containing a known amount of a reducible substance (*e.g.*, cadmium ion) for which $n$ is known: if the diffusion currents in the two electrolysis cells are measured separately before and after the electrolysis, it is possible to obtain the ratio of the number of moles of unknown substance reduced to the number of moles of standard substance reduced by the same quantity of electricity, and this immediately gives the ratio of $n$-values.

Each of these techniques involves the danger of mechanical loss of an appreciable fraction of the small volume of solution that must be employed. The first also involves errors due to local depletion of the solution around the tip of the dropping electrode; the others involve other errors which are associated with the explicit or implicit measurement of the quantity of electricity consumed during the electrolysis. These and other errors have been studied by WEAVER AND WHITNACK[5].

This communication describes a fourth technique, which requires the use of only a single dropping electrode, does not involve the use of any external apparatus for current integration, and avoids many of the errors encountered in these other techniques.

## THEORY

Assume that a solution contains two reducible substances, A and B, which yield polarographic waves corresponding to the half-reactions

$$A + n_A e \rightarrow A'$$
$$B + n_B e \rightarrow B'$$

Assume that the waves are sufficiently well separated on the polarogram to permit their diffusion currents to be measured separately. If the solution is electrolyzed with a dropping electrode whose potential is maintained at a value on the plateau of the total combined wave, a current will flow which is the sum of the diffusion currents of A and B, and each of these will be reduced at a rate proportional to its own diffusion current. If it is further assumed that the diffusion current of each is proportional to its concentration by a proportionality constant *k*, then the rate of change of concentration of A will be given by

$$-\frac{dC_A}{dt} = \frac{i_{d_A}}{n_A F_y V} = \frac{k_A C_A}{n_A F_y V} \tag{1}$$

Integration and obvious substitutions yield

$$\log\,(i_{d_A}/i^\circ_{d_A}) = -\frac{0.4343\, i^\circ_{d_A}}{n_A F_y V C^\circ_A}\, t \tag{2}$$

where superscript zeros refer to the initial solution. Dividing this by the corresponding equation for B and rearranging,

$$\frac{\log\,(i^\circ_{d_A}/i_{d_A})}{\log\,(i^\circ_{d_B}/i_{d_B})} = \frac{i^\circ_{d_A} n_B C^\circ_B}{i^\circ_{d_B} n_A C^\circ_A} \tag{3}$$

in which the units are obviously immaterial as long as they are consistent. As the volume of solution does not appear in this equation, it need not be known, and losses (*e.g.*, by entrainment into the gas stream used for deaeration and stirring) are without effect. Errors due to local depletion of the solution around the capillary tip are nearly eliminated by the fact that they will affect A and B about equally.

What is required experimentally is that a solution containing known concentrations of a substance, A, for which *n* is to be determined, and of a second substance, B, for which *n* is known, be electrolyzed with a dropping electrode at a potential on the plateau of the second wave for a length of time sufficient to decrease both concentrations appreciably. The diffusion currents of A and B are measured initially and again at the end of the electrolysis, and $n_A$ is then calculated from eqn. (3). This is a considerably simpler technique than any of those previously proposed.

The crucial chemical requirement is that neither of the products of the electrode reactions must be capable of reacting with either of the starting materials in any way that will lead to a change in the measured diffusion currents. In practice, this includes (but is not limited to) a requirement that the second wave be totally irreversible; satisfactory results are often impossible, and always difficult, to secure if this is not the case. Several examples of chemical interactions between products and starting materials that lead to erroneous results will be cited below, and it will be apparent that a judicious selection of the "pilot" ion is essential to success.

## EXPERIMENTAL

Solutions containing known concentrations of two reducible substances were prepared from stock solutions which had been standardized by conventional methods.

From 0.25 to 0.50 ml of a mixture was placed in the dropping-electrode compartment of a micro H-cell[6] and deaerated with a slow stream of prepurified nitrogen which had been scrubbed with chromous chloride and then with water. When deaeration was judged to be complete, the dropping electrode was inserted and a polarogram was recorded. By appropriate adjustment of the bridge of the polarograph, a potential was then applied which was near the center of the plateau of the second wave on the polarogram, and the electrolysis was allowed to proceed for 1–2 hours with a stream of nitrogen flowing over the surface of the solution. At the end of this time, the solution was stirred briefly with nitrogen, and a second polarogram was recorded.

During the recording of each polarogram there is an interval during which only the substance responsible for the first wave is being reduced. As this is not taken into account in the derivation of equation (3), it causes the calculated value of $n$ for that substance to be a little too high. Hence the electrolysis interval should be much longer than the time during which the first wave is recorded on the polarogram. Moreover, the logarithmic nature of eqn. (3) is such that the normal experimental errors of measuring the diffusion currents will lead to a fairly large relative error in the calculated value of $n$ unless the electrolysis is allowed to proceed until at least about 50% of each reducible substance has been consumed.

A conventional pen-and-ink recording polarograph was used; in view of the considerations just outlined, care was taken to obtain all polarograms as rapidly as possible. All measurements were made at 25.00 ± 0.01°.

## DATA AND DISCUSSION

A typical example of a successful application of the proposed technique is that in which the two reducible substances are thallium(I) and nickel(II). In one experiment a solution containing 2.05 m*M* thallous ion, 1.99 m*M* nickel ion, 0.005% gelatin, and 1 *F* sodium perchlorate was electrolyzed for 60 min at —1.4 V *vs.* S.C.E. During this time the diffusion current of thallous ion decreased from 12.65 to 6.75 $\mu$A, while that of nickel ion decreased from 14.51 to 9.84 $\mu$A. Substituting these values, together with $n_{\mathrm{Tl}} = 1$, into equation (3) yields $n_{\mathrm{Ni}} = 1.91$. A similar experiment with an ammoniacal ammonium chloride supporting electrolyte gave $n_{\mathrm{Ni}} = 1.95$. The small deviations from the expected value of 2 can be attributed to errors of the order of ±1% in the measurements of the four diffusion currents. As is usually the case in coulometric experiments with dropping electrodes, the precision of the result increases with increasing extent of depletion of the solution; hence it is advantageous to prolong the electrolysis as much as possible.

An example of an interaction between starting material and electrolysis product that does not affect the calculated $n$-value is that which occurs in the following experiment. A solution initially containing 2.00 m*M* copper(II) and 2.04 m*M* iodate in 0.1 *F* ammonia —0.1 *F* ammonium oxalate was electrolyzed at —1.40 V *vs.* S.C.E. for 2 h. The total diffusion current of the double wave representing reduction of copper to the amalgam decreased from 15.35 to 9.70 $\mu$A, while the diffusion current of iodate decreased from 46.9 to 29.3 $\mu$A. These data give $n_{\mathrm{IO_3^-}} = 5.82$. However, both the polarogram and the color of the solution at the end of the electrolysis indicated that the reaction $\mathrm{Cu(Hg)} + \mathrm{Cu(II)} \rightarrow 2\ \mathrm{Cu(I)}$ between the amalgam and the copper(II) which escaped electrolytic reduction had occurred to a considerable extent. The nearly correct value of $n$ obtained from the experiment reflects the fact that the copper(I) produced by this reaction gave a diffusion current almost identical with the diffusion current of the copper(II) that the reaction consumed.

At the other extreme, an interaction that does alter the *n*-value was encountered in experiments with solutions containing lead and cadmium ions. When a solution containing 3.97 m*M* lead and 5.00 m*M* cadmium was electrolyzed for 1 h at a potential on the plateau of the cadmium wave, the diffusion current of lead ion decreased from 40.0 to 13.5 $\mu$A while the diffusion current of cadmium ion decreased from 44.8 to 36.0 $\mu$A. Taking $n_{Cd} = 2$, these data give $n_{Pb} = 0.45$. The error is due to the reaction $Cd(Hg) + Pb^{++} \rightarrow Cd^{++} + Pb(Hg)$, which occurs primarily, though not exclusively, at the surface of the dilute cadmium amalgam that collects at the bottom of the cell. When the experiment was repeated with a layer of chloroform to protect the amalgam, and when the tip of the dropping electrode was placed almost in contact with the surface of the chloroform, a value of 1.97 was obtained for $n_{Pb}$. On the other hand, with the tip of the dropping electrode 1 cm above the chloroform, the value obtained was $n_{Pb} = 1.81$, showing that the above reaction occurs to an appreciable extent during the brief interval between the detachment of a drop from the capillary tip and its entrance into the protective layer of chloroform. Protecting the pool of reaction product with a layer of chloroform is a simple and useful expedient in dealing with metal amalgams; unfortunately it is useless when, as is true in organic systems, the products of the electrode reactions remain in the solution phase.

It is clear that much discretion must be exercised in choosing the pilot substance and in guarding against deleterious side reactions. When this is done, however, the convenience of the technique and its comparative immunity to mechanical sources of error should commend it to the attention of those seeking to determine polarographic *n*-values by electrolyses with dropping mercury electrodes.

## SUMMARY

The theory and the experimental and chemical requirements of pilot-ion coulometry with the dropping mercury electrode are outlined, and several examples are given of its application to the determination of *n*-values for half-reactions occurring in polarographic experiments.

## RÉSUMÉ

Une nouvelle méthode par mesures coulométriques ("pilot-ion coulometry") est décrite pour la détermination des valeurs de *n* en polarographie, avec électrode à gouttes de mercure.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über "Pilot-Ion" Coulometrie mit einer Quecksilbertropfelektrode. Das Verfahren dient zur Bestimmung polarographischer *n*-Werte.

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# Book reviews

*Gas Chromatography, 1960*, by R. P. W. Scott (Editor), Butterworths, London, 1960, xvii + 466 pp., 95s.

This volume contains the proceedings of the third symposium organised by the Society for Analytical Chemistry and the Gas Chromatography Discussion Group of the Institute of Petroleum, held in Edinburgh in June 1960. Twenty-nine papers were presented at the symposium. Many of these describe developments in the theory of, and construction of, capillary columns and of sensitive detectors, and demonstrate the significant advances made in these fields since the previous symposium. About half the papers describe the application of gas chromatography to specific problems, and their titles indicate the widespread appreciation of the value of gas chromatography in most branches of chemistry. Although the emphasis of the conference lay, not unreasonably, on the use of chromatography for analysis, it is encouraging to note one paper discussing factors involved in the construction of columns for preparative-scale chromatography.

This book should be available to all who are interested in gas chromatography, and in these days this means the majority of chemists. It is to be regretted, of course, that the proceedings of these excellent symposia as separate volumes has become established practice. The papers could more appropriately be published in available journals, as this would cause less confusion in an already overloaded literature.

C. R. Patrick (Birmingham)

*Anal. Chim. Acta*, 25 (1961) 97

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*Qualitative Analysis and Electrolytic Solutions*, par Edward J. King, Harcourt, Brace and Company, New York, 1959, xxi + 641 pp., $ 7.25.

Le livre, que nous avons le plaisir de présenter aux lecteurs des "*Analytica Chimica Acta*", est composé des chapitres suivants: Water; An Introduction to Solutes and Solutions; Ionic Reactions and Ionic Equations; The Concentration of Substances in Solution; More About Solutes and Solutions; Coordination Compounds; Reaction Rates and Chemical Equilibria in Solution; Precipitates and Colloidal Suspensions; The Direction of Reversible Ionic Reactions; An Introduction to Calculations with Equilibrium Constants; Acids and Bases; The Common Ion Effect, Buffer Solutions, Indicators; Solutions Containing Several Weak Acids and Bases; The Dissociation of Complex Ions; Electric Cells; The Laboratory Work in Qualitative Analysis; Cation Group 1; Cation Group 2; Cation Group 3; Cation Group 4; Cation Group 5; The Properties of Anions; The Identification of Anions; The Analysis of Solids for Cations and Anions; Special Methods of Qualitative Analysis; Appendixes.

La parution d'un nouveau manuel d'analyse qualitative pourrait laisser nos lecteurs

quelque peu indifférents, vu le nombre de publications déjà existantes dans ce domaine. Or, précisément, le livre en question est à prendre sérieusement en considération, étant donné son originalité.

En ce qui concerne la partie théorique, nous nous plaisons à reconnaitre que, peu à peu et en partant des notions les plus simples, l'auteur a su construire un édifice harmonieux qui s'érige jusqu'aux niveaux élevés de la chimie physique. (Nous ne citerons ici en exemple que le calcul des produits de solubilité à partir des énergies libres de formation). D'autre part, de bonnes références bibliographiques permettent aux étudiants intéressés d'étendre les connaissances acqùises par la lecture de cet ouvrage. Des nombreux schémas et illustrations aident le lecteur à se faire une idée plus tangible des notions théoriques. Grâce à de petits artifices d'écriture l'étudiant se rend compte quels sont les facteurs importants et quels sont les facteurs secondaires dans un calcul. Des exemples de calculs approximatifs et exacts sont également donnés avec une clarté qui est tout à l'honneur de M. King.

Quant à la partie pratique, elle est aussi satisfaisante. Elle est essentiellement classique, avec quelques heureuses modifications dictées par les acquisitions récentes de l'analyse chimique.

L'impression du livre est impeccable et en facilite grandement la lecture. Nous recommandons donc vivement cet ouvrage dont l'introduction aux Universités Européennes serait à souhaiter.

I. Kapétanidis (Genève)

*Anal. Chim. Acta*, 25 (1961) 97–98

*Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique*, publiées sous la direction de J. A. Gautier, 8e série, 148 pages (16.5 × 25), 14 figures et 8 tableaux, Masson et Cie, Paris, 1960, 26 NF.

La collection dont je lis et analyse régulièrement les Conférences, continue sa bonne voie. Avec un recul de 8 ans, on se rend compte qu'elle répond à un réel besoin. Le succès est dû, nous le savons, au choix des sujets traités et, naturellement, de la notoriété des conférenciers, à la bibliographie intelligente et à une présentation agréable.

Cet ouvrage annuel contient cette fois une mise au point de P. Chovin sur la chromatographie en phase gazeuse (appareillage, bases théoriques, température, phase stationnaire, etc.). L'auteur cite quelques applications corps gras, hydrocarbures, matières colorantes, aromes. La deuxième Conférence due à A. Desvignes a pour titre: Les possibilités de l'analyse par voie microbiologique. Les micro-organismes se comportent comme de véritables réactifs spécifiques dont on peut suivre 'la multiplication ou l'inhibition, la modification des activités métaboliques (dosage des hormones). L'auteur insiste sur les difficultés opératoires: choix et conservation des souches. Ensuite, P. Devillers décrit en détail l'analyse bactériologique des sucres; il fait la critique des résultats, précise les normes, les origines et les remèdes aux contaminations. Puis, F. Percheron expose les méthodes chimiques et physiques de dosage des groupements C-méthyle et l'identification des chaînes alcoylées dans les matières organiques. L'ouvrage se termine par une intéressante étude de G. Le

*Anal. Chim. Acta*, 25 (1961) 98–99

Moan (avec 232 références) des problèmes posés par l'emploi des pesticides en agriculture. L'auteur donne le dosage de résidus toxiques dans les aliments et les sols et celui d'un grand nombre de pesticides minéraux et organiques.

Cl. Duval (Paris)

*Anal. Chim. Acta*, 25 (1961) 98–99

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*The Identification of Organic Compounds* by Stig Veibel, 5th Ed., 2nd English Ed., G.E.C. Gad, Copenhagen, 1961, xvi + 426 pp.

It is just over six years since the first English edition of this book appeared. During this time, many new developments have been made in the field of study covered by this book and it is proper that a new edition should now have been prepared.

Professor Veibel's work in the field of organic functional group analysis needs no elucidation or recommendation from this reviewer; his active researches in this branch of organic analysis have earned him a world-wide reputation which this new edition can only enhance. The book retains the form and system of the 1954 edition, but it has undergone appreciable revision, particularly with regard to the use of new and better reagents for several functional groups, and the means of determining the equivalent weights of the various derivatives used to establish the identity of the unknown compounds. The extended use of non-aqueous titrimetry has led to the improvement of many procedures for the determination of organic compounds. Many of these are now incorporated in the present text. The major part of the book is concerned with the identification of functionality in organic compounds through the formation of specific derivatives and their quantitative analysis — an approach to the subject of organic analysis at which Professor Veibel excells. In contrast, however, the early chapter on ultimate analysis, both qualitative and quantitative, lacks details or even mention of the many excellent new tests and analytical methods which have come to the fore in recent years. Obviously these aspects of organic analysis form a minor part in the purpose of the present text.

In conclusion, this book cannot be too strongly recommended to all interested in organic analysis. It contains a wealth of information (over 400 pages of text in what appears to be a very modestly sized book), and it is well indexed. The errors which have been noted are mainly typographical and in no way alter the chemical sense of the text.

W. I. Stephen (Birmingham)

*Anal. Chim. Acta*, 25 (1961) 99

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*Die Flammenspektralanalyse*, von W. Schuhknecht, Bd. 48 der Reihe: *Die chemische Analyse*, Ferdinand Enke, Stuttgart, 1961, 258 Seiten, 42 Abbildungen, 67 Tabellen.

Die spektrochemische Analyse mit Flammenanregung, an sich seit mehr als 100 Jahren bekannt, hat in den letzten 15 Jahren eine stürmische Entwicklung durchgemacht. Nicht nur die Anwendungsmöglichkeiten und die Leistungsfähigkeit der auf diesem Prinzip beruhenden Verfahren, sondern auch die Zahl derer, die sich dieser Methoden bedienen haben sich in dieser Zeit erheblich vergrössert. Neben

***Anal. Chim. Acta*, 25 (1961) 99–100**

einer grossen Zahl von Einzelveröffentlichungen über dieses Gebiet, die wohl über 3000 liegen dürfte, sind auch eine Reihe zusammenfassender Darstellungen und Bücher erschienen, welche dem Bedürfnis derer Rechnung tragen, die sich neu in flammenspektralanalytische Verfahren einarbeiten wollen. Auch das hier vorliegende Buch von Schuhknecht ist nicht als vollständige und erschöpfende Darstellung des Gesamtgebietes gedacht sondern als Einführung in und als Hilfe für das praktische Arbeiten. Dementsprechend steht die Beschreibung und Diskussion der wesentlichen Vorgänge, Einrichtungen, Arbeitsprinzipien und Fehlermöglichkeiten im Vordergrund, in einem Umfange, wie es für ein verständnisvolles Arbeiten erforderlich ist und nicht die referierende Behandlung der Literatur. Dabei ist weitgehend auf die eigenen Arbeiten des Verfassers Bezug genommen worden, der sich seit mehr als 25 Jahren mit der Flammenspektralanalyse praktisch beschäftigt und wesentliche Beiträge zur Entwicklung der Methode geliefert hat, die besonders auf apparativem Gebiet und im Bereich der Anwendung auf praktische Fragen liegen aber auch dem Studium einiger theoretischer Fragen gewidmet sind.

Zunächst werden die Zerstäuberbrenner und ihr Betrieb (30 Seiten) und die Anregung in der Flamme (34 Seiten) besprochen, danach Bau und Arbeitsweise der Flammenphotometer und Flammenspektralphotometer (33 Seiten), wobei ihre Vor- und Nachteile gegeneinander gehalten werden. Es folgt eine allgemeine Beschreibung der Arbeitstechnik und -methodik (21 Seiten). Besonders ausführlich ist das Kapitel Flammenphotometrische Arbeitsvorschriften gehalten (74 Seiten), in welchem die Bestimmung der Alkali- und Erdalkalimetalle unter Verwendung des vom Verfasser entwickelten Gerätes in verschiedenen Materialien in allen Einzelheiten beschrieben wird und Hinweise für die Bestimmung anderer Elemente, auch eniger Nichtmetalle, gegeben werden. Ein Abschnitt über Flammenspektrographie (18 Seiten) und ein Literaturverzeichnis (496 Zitate) schliessen das Buch ab.

Das Buch kann als gute Grundlage zur Einarbeitung in die Flammenspektralanalyse empfohlen werden, aber auch dem Erfahreneren wird mancher aus der Praxis gegebene Hinweis von Nutzen sein.

H. Bode (Hannover)

*Anal. Chim. Acta*, 25 (1961) 99–100

## Publications received

1. *Contributi Teorici e Sperimentali di Polarografia*, Vol. V, 1960, Supplement to *La Ricerca Scientifica*, A cura del Centro di Studio per la Polarografia, Price: 2500 lire, 315 pp.
2. *Bibliografia Polarografica (1922–1959)*, Part I (1958) and Part II (1960), Supplement to *La Ricerca Scientifica*, A cura del Centro di Studio per la Polarografia, Price: 800 lire and 1,000 lire, 80 and 63 pp.
3. *Reagent Chemicals: American Chemical Society Specifications, 1960*, prepared by the 1960 Committee on Analytical Reagents (chairman: W. Stanley Clabaugh), Applied ublications, American Chemical Society, Washington, D.C., 1961, xv+564 pp.
4. *Chimie générale et abrégé de Chimie minérale*, par P. Colmant, Masson et Cie, Paris, 1960, 566 pp., 96 figs., Price: NF 45.

*Anal. Chim. Acta*, 25 (1961) 100

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
## Vol. 25, No. 2, August 1961

### ANALYSIS OF ALIPHATIC ALDEHYDES IN SOURCE EFFLUENTS AND IN THE ATMOSPHERE

*(Review)*

A. P. Altshuller, I. R. Cohen, M. E. Meyer and A. F. Wartburg Jr., *Anal. Chim. Acta*, 25 (1961) 101–117

### RELATIVE DATA OF CHEMICAL EQUILIBRIA GOVERNING THE SEPARATION OF ZIRCONIUM FROM HAFNIUM

PARTS II AND III

*(in French)*

The chemical equilibria governing the separation of zirconium from hafnium are considered with particular reference to the solvent. The conditions of separation of a mixture of tributylphosphate, diluent and zirconium have been studied as well as the interaction of tributylphosphate and zirconium. The latter results in the formation of dibutylphosphate which has a strong complexing capacity for zirconium.

J. Huré, M. Rastoix and R. Saint-James, *Anal. Chim. Acta*, 25 (1961) 118–128

### ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co

II. SOLVENT EXTRACTION

Extractions with acetylacetone and diethyldithiocarbamate are described. Through the sucessive application of these reagents the constituents of biological ashes are concentrated and separated into the groups: *(1)* $MoO_4^{-2}$, *(2)* $Fe^{+3}$, $Cu^{+2}$, *(3)* $Mn^{+2}$, *(4)* $Zn^{+2}$, *(5)* $Pb^{+2}$, *(6)* $Co^{+3}$ and *(7)* $Na^{+}$, $K^{+}$, $Ca^{+2}$, $Mg^{+2}$, $SO_4^{-2}$, $PO_4^{-3}$.

P. C. van Erkelens, *Anal. Chim. Acta*, 25 (1961) 129–135

### INDIRECT OXIDIMETRIC DETERMINATION OF CERTAIN α-AMINO ACIDS WITH VANADIUM(V)

A method for preparing standard vanadate solution using pure vanadium pentoxide as primary standard is described. The determination of certain α-amino acids by oxidation of their de-amination products with standard vanadate solution is studied.

S. P. Rao, H. S. Rathi and J. N. Gaur, *Anal. Chim. Acta*, 25 (1961) 136–138

## QUANTITATIVE ASPECTS OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY POTASSIUM PERMANGANATE

### I. METHANOL AND ETHANOL

The quantitative oxidation of methanol and ethanol by acidified potassium permanganate solution has been studied. Molybdate is superior to manganese(II) as the catalyst. In fairly dilute methanol solutions a large excess of permanganate oxidises the alcohol quantitatively to carbon dioxide. With ethanol, oxidation proceeds beyond the acetic acid stage but the further reaction is not stoichiometric.

J. SHARP, *Anal. Chim. Acta*, 25 (1961) 139–145

## 1,8-DIHYDROXYANTHRAQUINONE AS A REAGENT FOR BORIC ACID AND ITS USE IN THE ANALYSIS OF PHARMACEUTICAL GRADE GLASS

1,8-Dihydroxyanthraquinone is proposed as an organic reagent for boric acid. The color change obtained is more useful for the determination of boric acid than those with other reagents of the anthraquinone group. The method is applied to the determination of boric acid transfers from pharmaceutical grade glass.

R. RUGGIERI, *Anal. Chim. Acta*, 25 (1961) 145–149

## APPLICATIONS OF THE CHELATOMETRY

### VI. VOLUMETRIC DETERMINATION OF *vic*-DIOXIMES

*(in French)*

*Vic*-dioximes can be easily determined by precipitation with a nickel salt, excess of which is titrated with EDTA.

C. HENNART, *Anal. Chim. Acta*, 25 (1961) 150–152

## A NEW REAGENT FOR THE DETECTION AND GRAVIMETRIC DETERMINATION OF SODIUM

5-Benzaminoanthraquinone-2-sulphonic acid is recommended as a reagent for the precipitation of sodium. It is the most sensitive precipitant for sodium yet proposed, being able to detect 5 $\mu$g of sodium at a limiting dilution of 1 in $4 \cdot 10^5$. The reagent is not selective and is unable to tolerate the presence of the other alkali metals and the ammonium ion. The use of the reagent for the gravimetric determination of 1.40–25.0 mg of sodium is described.

H. S. GOWDA AND W. I. STEPHEN, *Anal. Chim. Acta*, 25 (1961) 153–158

## THERMOGRAVIMETRIC ANALYSIS OF METALLIC QUINALDATES

*(in French)*

Thermogravimetric analysis is used to determine the hydration of metallic quinaldates, as well as the thermal stability of the anhydrous quinaldates and of the water of hydration. Deductions are made with regard to structure by comparison with results previously obtained for oxinates and picolates.

G. THOMAS AND R. A. PÂRIS, *Anal. Chim. Acta*, 25 (1961) 159–165

## A SENSITIVE NEW METHOD FOR THE DETERMINATION OF NITRITES AND NITROGEN DIOXIDE WITH 4-AMINOAZOBENZENE-1-NAPHTHYLAMINE

A sensitive method for the determination of nitrites is proposed. The method should also be applicable to the determination of nitrogen dioxide. The test consists of the reaction of 4-aminoazobenzene and 1-naphthylamine with nitrous acid to form the blue di-cation of 4-(*p*-phenylazophenylazo)-1-naphthylamine. Beer's law was obeyed from 0.5 to over 15 $\mu$g of nitrite ion per 15 ml of final solution. Spectrophotometrically it is possible to detect 1 part of nitrite ion in 60 million parts of solution.

E. Sawicki and J. L. Noe, *Anal. Chim. Acta*, 25 (1961) 166–169

## A MODIFIED TRITIUM GAS COUNTING PROCEDURE

The Wilzbach one-step method for tritium analysis has been re-investigated because of difficulty in obtaining satisfactory results with the available catalysts. The important factors governing the conversion of tritium from an organic compound to the gaseous phase have been studied. Such factors include the use of zinc dust instead of zinc mesh for the reduction step, temperature of combustion, and the effect of variation in catalyst weight and sample size on conversion efficiency.

J. L. Garnett, W. K. Hannan and S. W. Law, *Anal. Chim. Acta*, 25 (1961) 170–175

## *p*-(3-HYDROXY-3-PHENYLTRIAZENO)-PHENYLTRIMETHYLAMMONIUM CHLORIDE AS A NEW COLOUR REAGENT FOR CERTAIN METAL IONS

The synthesis and qualitative reactions of *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride are described. The solubilising effect of the quarternary ammonium group is studied; this group is valuable for the conversion of organic precipitants to colorimetric reagents.

J. N. Gaur, N. K. Mathur and D. C. Sancheti, *Anal. Chim. Acta*, 25 (1961) 176–178

## THE DETERMINATION OF FLUORIDES IN NATURAL WATERS, WITH PARTICULAR REFERENCE TO SEA WATER

The chelate formed between lanthanum and alizarin complexone has been used as the basis of a method for the determination of fluoride in natural waters, with special reference to sea water. The fluoride complex formed with the reagent is developed rapidly at pH 4.50 by the addition of a single buffered reagent and is stable for several days. The fluoride complex is formed in 16% v/v acetone solution; the acetone stabilises the reagent and increases its sensitivity to 0.0018 $\mu$g/cm$^2$. Beer's law is followed up to *ca.* 25 $\mu$g of fluoride. The interference of inorganic ions present in natural waters has been investigated. Abnormally large amounts of aluminium interfere seriously, but can be removed by extraction as its oxinate in a continuous extractor. For sea water of chlorinity within the range 15 to 20‰ the salt error correction is constant and equal to 4.0%. The method showed a coefficient of variation of 0.3% with a sea water containing 1.37 $\mu$g of fluoride/ml.

R. Greenhalgh and J. P. Riley, *Anal. Chim. Acta*, 25 (1961) 179–188

## DETERMINATION OF SILICA IN IRON ORE

A rapid and reliable routine method for determination of silica in iron ore has been developed and tested. The silica is converted to potassium fluosilicate by digestion with hydrofluoric acid, hydrochloric acid and potassium chloride and determined volumetrically.

Ö. GLASÖ AND G. PATZAUER, *Anal. Chim. Acta*, 25 (1961) 189–192

## THE SEPARATION AND PHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM

A study was made on the extraction of hexavalent chromium from hydrochloric acid solutions with methyl isobutyl ketone. Quantitative extraction was accomplished from 3 *N* hydrochloric acid with 25 ml of solvent. Under these conditions, it was found that chromium could be extracted from vanadium. A procedure was developed for the colorimetric determination of chromium in the ketone phase and of vanadium in the aqueous phase. The analytical procedure was used to analyze standard steel samples for chromium and vanadium, and the results obtained by this method were found to agree with the accepted values.

S. A. KATZ, W. M. MCNABB AND J. F. HAZEL, *Anal. Chim. Acta*, 25 (1961) 193–199

## A NEW SPECIFIC TEST FOR ALUMINIUM

A new specific spot test for aluminium is described. The test is based on the demasking action of aluminium ion on calcium fluoride, and subsequent detection of the liberated calcium by glyoxal bis-(2-hydroxyanil).

E. JUNGREIS AND A. LERNER, *Anal. Chim. Acta* 25 (1961) 199–201

## APPLICATIONS OF THE CHELATOMETRY

### XIV. VOLUMETRIC DETERMINATION OF *vic*-DIKETONES

*(Short Communication; in French)*

C. HENNART, *Anal. Chim. Acta*, 25 (1961) 201–202

## POTENTIOMETRIC TITRATION OF THALLIUM(III) WITH CHROMIUM(II) SOLUTION

*(Short Communication)*

R. MAJUMDAR AND M. L. BHATNAGAR, *Anal. Chim. Acta*, 25 (1961) 203–204

**Review**

# ANALYSIS OF ALIPHATIC ALDEHYDES IN SOURCE EFFLUENTS AND IN THE ATMOSPHERE

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(Received February 7th, 1961)

Aldehydes have been identified in various combustion sources including automobile exhaust[1-4], diesel engine exhaust[5], and incinerator effluents[1,6-8]. Cooking of oils and varnishes in the paint and varnish industry and baking of molds in iron foundries are among the other sources producing significant amounts of aldehydes[9]. Several laboratory investigations have shown that aldehydes are major products from the photooxidation of olefin-nitrogen oxide mixtures[10,11].

Eye irritation appears to be a highly complex phenomena attributable to a number of gaseous species possibly adsorbed on aerosol particles. However, aldehydes such as formaldehyde and acrolein generally are considered to contribute a significant part of the total eye irritation[10,11]. Upper respiratory and malodorant effects also have been attributed to aldehydes[6,12].

Irradiation of aldehydes has been reported to produce phytotoxicants which damage petunias and bean plants in the same way as do the products of irradiated hydrocarbon-nitrogen oxide mixtures[11]. Such irradiated mixtures cause plant injury indistinguishable from the damage caused by the phytotoxicants in polluted air[11].

Since only formaldehyde and $\alpha,\beta$-unsaturated aldehydes of all the aldehydes have been shown to be eye irritants in the part per million range, methods of analysis for these compounds are of particular interest. Plant damage effects may be produced by irradiation of saturated aldehydes, since $\alpha,\beta$-unsaturated aldehydes do not photolyze significantly. Consequently, methods for total aliphatic aldehydes might be useful. It has been suggested that higher saturated aldehydes are highly unstable in air. While this conclusion is not supported by other laboratory evidence, it might be of interest to have a method for total higher saturated aldehydes. It is easier to cite needs for such methods than to develop sensitive and specific methods for particular compounds or subclasses of aldehydes. At present, colorimetric methods appear to be the most generally usable for analysis of combustion sources and the atmosphere. Polarographic procedures have been very useful in analyzing for aldehydes and formaldehyde in cool flame products and in some atmospheric work[13,14]. Acrolein and crotonaldehyde have been analyzed in cool flame products and in products of the cooking of oils and the baking of molds in iron foundries[9,13,15]. However, polarographic methods have not been widely applied to air pollution problems. In part this may result from the lack of polarographic equipment in many laboratories. Gas chromatography and infrared spectroscopy certainly can be employed in analyzing for aldehydes in simplified systems[10,11,16–18], but are difficult to apply to aldehyde analysis in complex combustion effluents or the atmosphere.

## METHODS OF ANALYSIS OF TOTAL ALDEHYDES

The method most widely used in practice to analyze for "aldehydes" is the bisulfite procedure[19,20]. In this method an addition complex is formed between the aldehyde and the bisulfite compound, the excess bisulfite is destroyed, the addition compound decomposed, and the bisulfite ion released is titrated with standard iodine solution. Actually, both aldehydes and some ketones are determined by this method. Although formaldehyde, acetaldehyde and propionaldehyde may be efficiently collected and determined, it is generally more difficult to analyze quantitatively for ketones by this method[21,22]. While the method has sufficient sensitivity for combustion effluent analysis, the limit of sensitivity often is being pressed in using the method to determine concentrations in the tenths of a p.p.m. range in the atmosphere[19,21].

All of the above factors tend to make the "aldehyde" concentrations determined by the bisulfite procedure somewhat uncertain. Obviously when large amounts of ketones exist in the combustion effluent or the atmosphere, the "aldehydes" determined will be higher than the true concentration of aldehydes. If significant amounts of ketones are present but the sampling is done at room temperatures or above, and at flow rates of 0.1 c.f.m. or higher, then some losses of ketones and of $C_4$ and higher aldehydes can result[21]. If only one or two impingers are used under these conditions even more serious losses may occur. Preferably, collection should be at about one liter per min into a series of three impingers placed in an ice bath. However, it also is possible that the degree of accuracy to be expected from the method in air pollution applications is insufficient to warrant all of the refinements mentioned. Whatever may be the limitations of this method, it is the only one which has been used in most investigations for aldehydes in combustion sources or in the atmosphere.

An argentimetric method using silver nitrate or silver oxide is quite specific for aldehydes, and it has some application for aldehyde analysis in combustion gases[4,23]. The procedure, which involves titration of the silver salts with thiocyanate, is rather lengthy. The sensitivity is low, so the method is unlikely to be of any use in atmospheric analysis.

Another volumetric procedure which can be utilized involves oxidation of the aldehydes to the corresponding acids with hydrogen peroxide in *alkaline* medium[4,24]. This method also is of limited sensitivity. It also may be applied to combustion gases but is of too low a sensitivity for atmospheric analysis.

An interesting polarographic method of aldehydes has been developed based on reduction of their semicarbazide derivatives[14]. Both aldehydes and ketones form such derivatives, but their half wave potentials are sufficiently different to permit a separate estimate of aldehydes and ketones. A small number of atmospheric measurements were made using this method. It might also be possible to determine the aldehydes directly in an appropriate electrolyte solution. Formaldehyde, $\alpha,\beta$-unsaturated aldehydes, and $C_2$ and higher saturated aldehydes might be determined separately and then summed. Such a procedure should be applicable to combustion gases or other effluents containing large amounts of aldehydes[13,15]. Since deoxygenation usually is essential, volatile aldehydes may be swept out of solution. Also, in very complex combustion or atmospheric gas mixtures smearing out of the polarograms may effect adversely the quantitative accuracy.

Infrared spectroscopy is of only limited applicability to aldehyde analysis in complex gas mixtures. The carbon-hydrogen stretching vibration of aldehydes at 3.6 $\mu$ has been of some use for aldehyde analysis in combustion gases or the atmosphere. While irradiated mixtures of individual hydrocarbons and nitrogen oxides can be analyzed for aldehydes by infrared methods, infrared spectroscopy only can be used to obtain an estimate of total aldehydes in more complex mixtures[25]. Of course, infrared analysis is very useful for other compounds, *i.e.*, olefins, ozone, organic nitrogen compounds, carbon monoxide, etc.

At present, it is difficult to determine aldehydes by gas chromatography in complex combustion mixtures[16,18]. A number of the aldehydes are poorly resolved from other oxygenated compounds and hydrocarbons on the columns available[18]. Identification may often be possible, but accurate quantitative analysis is difficult[16,18]. Although gas chromatography has a considerable potentiality for oxygenate analysis, much additional investigation is needed for its effective application to air pollution problems.

A combination of gas chromatography and infrared spectroscopy is much more effective than either method separately. Chromatographic separations which reduce the fractions going to the infrared instrument to two or three components make qualitative verification and quantitative analysis possible. Of course, sufficient material must be collected to be well above the sensitivity limits on the infrared equipment. Such a combination of techniques is powerful, but it is also expensive and time-consuming. While more detailed information may result, it also is possible that the essential composition data may be obtained more rapidly and inexpensively from other techniques such as colorimetric methods of analysis. This is not a criticism of such instrumental techniques. It is merely a suggestion that they are at present far more useful as research tools for a very limited number of highly detailed analyses, rather than as methods applicable to routine or semi-routine analysis.

A wide variety of color tests for aldehydes has been proposed. These tests are adequately reviewed elsewhere[22,26]. Only a few of these tests have adequate specificity, sensitivity and quantitative reproducibility and accuracy to warrant consideration as quantitative procedures for total aliphatic aldehydes. Only the limited number of such methods will be considered in the present discussion.

Schiff's reagent is one of the oldest reagents used for aldehydes[26,27]. It is prepared from rosaniline hydrochloride (basic fuchsin) and sulfur dioxide. The quantitative procedure has many disadvantages. The sensitivity is less than that in the bisulfite method which makes it inadequate for atmospheric analysis[26]. The sensitivities of the products of various aldehydes vary considerably[27]. Furthermore, the linear relationship between absorbance and concentration is followed over only a narrow range of concentrations[27]. The rate of color formation varies depending on the aldehyde considered[26]. Finally, interference from sulfur dioxide, ethanol, acetone and similar compounds is appreciable[27]. All of these factors combine to minimize the utility of this method in air pollution applications.

Reaction with 2,4-dinitrophenylhydrazine to form a colored product is a widely used procedure for identification of aldehydes and ketones[27]. If it is used as an identification and analytical method following separation by column or paper chromatography, many individual aldehydes can be determined. However, such a procedure again is a research method satisfactory for the detailed analysis of a limited number of samples. Without separation it is difficult to analyze for the aliphatic aldehydes in the presence of ketones and aromatic aldehydes. In alkaline solution, aldehyde products show a rapid color fading[28]. Analysis by difference initially and after several hours might possibly prove useful except that the fading is not complete and ketone derivatives also fade, although not as rapidly[28]. Consequently, the method, without separation techniques, only gives a measure of total aliphatic and aromatic aldehydes and ketones present in a sample.

Recently a sensitive method for total aliphatic aldehydes has been presented[29]. The method depends on the reaction of aldehydes with 3-methyl-2-benzothiazolone hydrazone to finally form a blue cationic dye. Filter paper, silica gel as well as colorimetric procedures for liquid samples have been developed[29]. Aliphatic and aromatic ketones, aromatic aldehydes and phenols are reported not to interfere significantly. The method is sensitive enough to readily permit atmospheric analysis[29].

The problem with this method, as with many others, is the range of molar absorptivities for the products of various aldehydes. For example, the formaldehyde product has a molar adsorptivity of 65,000, the acetaldehyde product, 51,000, the 2-methylpropanal product, 23,000 and the acrolein product 23,000, all at an adsorption maximum near 670 m$\mu$[29]. In a complex mixture of unknown composition, the aldehyde content even if expressed in terms of formaldehyde is subject to significant uncertainty. This is a frequent problem in colorimetric analysis for whole classes of compounds. Overall, this method appears to have possibilities.

## METHODS OF ANALYSIS FOR FORMALDEHYDE

Several volumetric methods have some degree of specificity for formaldehyde. These include the potassium cyanide, hydrogen peroxide (mild oxidation) and ammonia procedures[27]. Of these three methods, the potassium cyanide method appears to be the most specific and it has been used to analyze for formaldehyde in automobile exhaust gases[4]. This method involves the reaction of the cyanide with the formaldehyde to form the cyanohydrin, conversion of the excess cyanide to silver cyanide with a known excess quantity of standard silver nitrate solution and finally the titration of the excess silver nitrate with thiocyanate[4,23]. The method has the limited sensitivity of the usual volumetric procedure, and it would be very difficult to apply it to the atmospheric analysis of formaldehyde.

Formaldehyde has been analyzed for polarographically in a number of simple mixtures[30,31] and in cool flame combustion products[13,15]. Polarograph determinations of formaldehyde have been reported to agree well with analyses made simultaneously by colorimetric methods[30]. It has been shown that polarographic analysis for formaldehyde should not be interfered with by acrolein, crotonaldehyde, acetaldehyde, propionaldehyde, methanol, formic acid, phenol, hydrogen peroxide or organic hydroperoxides[13,30,31]. No analyses appear to have been made for formaldehyde by polarographic methods on combustion effluents from automobiles or incinerators or on samples collected from urban atmospheres.

The infrared spectrum of formaldehyde is not particularly characteristic. In complex mixtures it is not possible to distinguish the C–H stretch or the carbonyl bond of formaldehyde from the overall absorption due to aldehyde and carbonyl compounds. Consequently, infrared spectroscopy alone does not appear to be useful for the identification and analysis of formaldehyde in combustion or atmospheric gas.

Considerable difficulty has been experienced in identifying formaldehyde by gas chromatography[16,18]. The compound or its polymer appears to be either irreversibly absorbed or covered by the water band in a number of attempts to identify it. Recently, it has been reported that formaldehyde has been detected and analyzed on a firebrick column coated with a surfactant[32]. Five and six carbon hydrocarbons probably would interfere in combustion or atmospheric mixtures even with use of multiple stage gas chromatography.

Several colorimetric procedures are available for the analysis of formaldehyde. Some of these procedures are both sensitive and specific enough to use for both complex combustion and atmospheric gases.

One of the earlier colorimetric methods used Schiff's reagent in acidic media[27]. Other aldehydes form colored products which fade much more rapidly than does the formaldehyde product. The formaldehyde product also fades slowly so the absorbance must be read shortly after acidification[22]. This procedure is not very sensitive, nor highly reproducible, and the procedure is subject to several interferences[22,27]. However, it is satisfactory for determining formaldehyde in some mixtures.

Among the reagents used in the analysis of formaldehyde, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) has a very high sensitivity[22]. This method has been widely used for the analysis of formaldehyde[33-35]. When the sulfuric acid content used is above 85% the product formed by chromotropic acid with formaldehyde is very stable, has a high color intensity, and obeys Beer's Law over a wide concentration range[34,35]. This procedure is both simple and rapid in its application to the analysis of formaldehyde either as a combustion effluent or as an atmospheric pollutant[35].

The interference situation for the chromotropic acid method has been investigated in detail. Such studies have not been made for most of the other analytical methods for aldehydes. It has been shown that mixtures of saturated aldehydes, ketones, methanol, ethanol, nitrogen dioxide and sulfites with formaldehyde do not affect the analysis by the chromotropic acid procedure[33-35]. Unsaturated aldehydes such as acrolein or crotonaldehyde, even if present in equal amounts with formaldehyde, interfere only slightly in this analysis[34,35]. Three carbon and higher straight-chain alcohols interfere slightly if present in large excess[35]. Branched chain alcohols interfere significantly if present in excess[35]. Olefins react with formaldehyde as do alcohols via the Prins reaction. Four carbon and higher olefins will interfere, but in gas mixtures, this interference can be minimized by appropriate collection conditions[35]. Aromatic hydrocarbons and phenols in excess of the formaldehyde concentration can interfere significantly[35]. The interference of aromatic hydrocarbons can be minimized by the proper collection medium, but phenols in excess will interfere generally with the analysis of formaldehyde by the chromotropic acid method[35]. It will be shown later in this work that, despite these interferences, the chromotropic acid method appears adequate for analysis of formaldehyde in situations of air pollution importance.

Formaldehyde can be determined as the formazan or its anion formed by reacting the aldehyde with a hydrazine, and oxidizing the product. Further reaction produces the formazan which can be converted to a highly colored anion. Phenylhydrazine has been used as the hydrazine and potassium ferricyanide as the oxidizing agent. The earlier procedures produced rather unstable products[30,36]. Other aldehydes interfered. An improved modification was reported which has been used to analyze for formaldehyde in automobile exhaust[37]. Recently a modification has been published which used 2-hydrazinobenzothiazole instead of phenylhydrazine as the reagent[38]. The product formed appears to be more intensely colored and more stable than the product formed in the phenylhydrazine procedures. In contrast to the chromotropic acid procedures which determines formaldehyde and substances which hydrolyze to formaldehyde in sulfuric acid, the hydrazine procedures are claimed to determine only formaldehyde[37].

## METHODS OF ANALYSIS FOR CONJUGATED UNSATURATED ALDEHYDES

Only a few chemical procedures have any specificity for unsaturated aldehydes such as acrolein, $\alpha$-methylacrolein or crotonaldehyde. Unsaturated aldehydes as a group may be determined by bromination[27], if other easily brominated species such as olefins and phenols are absent from the sample being analyzed. Such restrictions make bromination procedures of little use in air pollution applications. Unsaturated aldehydes, as well as other types of unsaturated oxygenates, can be analyzed by addition of excess dodecanethiol and titration of the excess mercaptan iodometrically[27].

The infrared bands characteristic of unsaturated aldehydes are overlapped by bands due to water vapor, other types of carbonyl compounds and some types of olefins. While it is possible to analyze for acrolein and other $\alpha,\beta$-unsaturated aldehydes in photolyzed mixtures of single diolefins with nitrogen oxides[10], it is not possible to determine unsaturated aldehydes by infrared spectroscopy in complex mixtures.

Unsaturated aldehydes can be analyzed in cool flame products of single hydrocarbons by polarographic methods[13,15]. Since the half-wave potentials of acrolein, $\alpha$-methylacrolein and crotonaldehyde are quite close to each other, it is doubtful that individual unsaturated aldehydes can be determined without preliminary separations. This is well realized by investigators using polarographic techniques. With preliminary separation as the 2,4-dinitrophenylhydrazones, acrolein and crotonaldehyde have been individually determined in cool flame products[15]. The applications to cool flame work involved mg quantities of aldehydes.

The polarographic method also has been applied to determine acrolein (and crotonaldehyde, if present) in mold burning in iron foundries and in cooking of oils and varnishes in the paint and varnish industry[9]. In these applications to situations in which the acrolein concentration was less than 1 p.p.m., the sampling and transfer procedure used was elaborate and time-consuming[9].

Acrolein, crotonaldehyde, and possibly $\alpha$-methylacrolein have been identified in automobile exhaust gases and cool flame products by means of gas chromatography[18]. Complete or nearly complete resolution of the unsaturated aldehydes from other oxygenated species is difficult to obtain[18]. Higher molecular weight aliphatic and aromatic hydrocarbons also interfere. Again, a combination of gas chromatography and infrared methods should make analysis possible.

Three colorimetric methods have been used for the analysis of acrolein. Tryptophan[39], phloroglucinol[40], and 4-hexylresorcinol[41,42] are used as color producing reagents in these methods. The tryptophan and phloroglucinol methods are insufficiently sensitive for analysis of acrolein in the p.p.m. range and below[42]. Appreciable interference results in these two procedures from the presence of excess amounts of other aldehydes, particularly formaldehyde, as well as from nitrogen dioxide and nitrates[42]. The 4-hexylresorcinol method has been applied to the analysis of raw, diluted and irradiated automobile exhaust gases, and also to a wide variety of liquid mixtures[42]. No significant interferences with the analysis of acrolein by the 4-hexylresorcinol method have been found in the applications investigated. The sensitivity of this procedure is such that less than one p.p.h.m. of acrolein readily can be detected[42]. The absorbance is linear with concentration of acrolein over a wide range[42].

Crotonaldehyde can also be analyzed using 4-hexylresorcinol method[43]. In contrast to the acrolein which forms a blue product with an absorption maximum at 605 m$\mu$, crotonaldehyde forms a product with its stronger absorption maxima at 385 and 345 m$\mu$. These bands may be used to analyze for crotonaldehyde in the presence of most aliphatic hydrocarbons, oxygenates and aromatics[43]. However, unsaturated compounds including $\alpha$-methylacrolein, 3-buten-2-one, furfural, and 1,3-pentadiene interfere somewhat if present in excess[43]. Acrolein interferes significantly in small quantities but the 605-m$\mu$ peak can be used to correct for the acrolein. More serious is the interference of nitrogen dioxide in the ultraviolet[43]. This interference restricts the application of the crotonaldehyde procedure to systems containing small or negligible amounts of nitrogen dioxide.

$\alpha$-Methylacrolein and furfural also can be identified, but not quantitatively analyzed by the 4-hexylresorcinol method. $\alpha$-Methylacrolein has an absorption maximum at 480 m$\mu$, while furfural has maxima[42] at 650, 550 and 445 m$\mu$.

## METHODS OF ANALYSIS FOR TOTAL HIGHER ALDEHYDES

No volumetric or infrared method is particularly applicable to the analysis of total higher aldehydes above formaldehyde. Polarographic procedures might be used. The available data indicate that unsaturated aldehydes, acetaldehyde and propanal and higher aldehydes might be determined separately and summed together[13,15,31]. Gas chromatographic techniques can be applied with the serious limitations discussed previously.

No colorimetric method is available for the direct determination of total higher aldehydes. Very few of the reactions which form colored products occur for higher aldehydes and not for formaldehyde. A sodium nitroprusside–secondary amine type reaction might have possibilities[22,26,44]. Recently, it has been shown that *p*-nitrobenzene-diazonium fluoborate in a phosphoric acid–2-methoxyethanol solvent medium reacts with propanal, acrolein and higher aldehydes, but not significantly with formaldehyde and acetaldehyde[45]. However, this reagent also reacts with ketones other than acetone.

The remaining alternative is to use a colorimetric method specific for formaldehyde, another method specific for total aldehydes, and subtract the values obtained to give total higher aldehydes. Obviously, the limitations in the two separate methods will make the difference in values only approximate. For example, assume that the chromotropic acid[33–35] or 2-hydrazinothiazole method[38] is used to determine formaldehyde, while the 3-methyl-2-benzothiazole method[29] is used for total aldehydes. Assume further that the distribution of atmospheric aldehydes actually is as follows: formaldehyde, 50 p.p.h.m.; acetaldehyde, 10 p.p.h.m.; propanal, 10 p.p.h.m.; butanal, 5 p.p.h.m.; 2-methylpropanal, 5 p.p.h.m.; pentanals, 5 p.p.h.m.; hexanals and higher aldehydes, 5 p.p.h.m.; acrolein, 5 p.p.h.m.; crotonaldehyde, $\alpha$-methylacrolein, glyoxal, 5 p.p.h.m. Using the absorptivities given for individual aldehydes, the 3-methyl-2-benzothiazolone procedure gives a concentration of 83 p.p.h.m. for "total aldehydes as formaldehyde". If the formaldehyde method used measures the actual formaldehyde concentrations as 50 p.p.h.m., then the apparent total higher aldehyde content will be 33 p.p.h.m. rather than 50 p.p.h.m. This 33% error is the result of the spread of three-fold in the absorptivities for individual aldehydes. This type of problem often will arise in the application of a colorimetric class analysis method to a complex mixture in air pollution studies.

## METHODS OF ANALYSIS FOR GLYOXALS

Volumetric, infrared and polarographic methods for glyoxal are either insufficiently sensitive, specific or accurate for the analysis of glyoxal. Gas chromatography may be applicable, but experimental data are not available.

A highly sensitive and apparently a very specific method for glyoxal has been reported based on its reaction with 2,3-diamino-phenazine to form pyrazino(*b*)-phenazine, an intensely blue-colored product[46]. Methylglyoxal also reacts but a much less intensely colored product is formed. This method even permits the analysis of glyoxal and methylglyoxal in the presence of diketones and hydroxyalkanals[46]. A less sensitive and specific procedure might be developed from the reaction of glyoxal with phenylhydrazine and potassium ferricyanide in acidic media to form a formazan absorbing at 375 m$\mu$ with a molar absorptivity[47] of 34,800. A sensitive fluorescent spot test for glyoxal also has been described recently based on the fluorescence products formed when glyoxal reacts with several reagents including 2-hydrazinobenzothiazole[48].

## PREVIOUS EXPERIMENTAL RESULTS ON SOURCE EFFLUENTS

Data are available on "aldehyde" concentrations from many sources including burning fuel gas, fuel oil, ovens, furnaces, steam boilers, incinerators and automobile exhaust[1-8]. Most of the data have been obtained using the bisulfite method and the values represent carbonyl content. The results are summarized in Table I. The values given can only be taken as roughly indicating the concentrations produced by the various combustion devices. Different devices of the same general type operating under differing conditions will give a fairly wide range of values. This is shown by the data available on domestic incinerators and automobile exhaust effluents. The results for the automobile must also be defined in more exact terms for the driving cycle, general engine and ignition conditions and for the fuel used. In one investigation aldehyde content was found to increase from 70 to 96 p.p.m. under cruising conditions as speed was increased from 15 to 60 MPH.

It is difficult to say how much of the so-called aldehyde reported in many of these investigations is ketone, which is also determined by the bisulfite method used. In one of the domestic incinerator studies made, acetone was determined separately by infrared methods as something under 260 $\mu$g/l, while the total carbonyl content ranged from 180 to 1960 $\mu$g/l in various runs[7]. The carbonyl content, as measured by three methods (hydroxylamine hydrochloride, sodium bisulfite, and 2,4-dinitrophenylhydrazine methods) on automobile exhaust, and the aldehyde content (alkaline hydrogen peroxide and argentimetric methods) did not differ significantly[4]. Furthermore, the methyl ketone content was very small. Whether higher aliphatic aldehydes have been collected effectively in many of these investigations also is difficult to ascertain.

TABLE I

ALDEHYDE CONTENTS OF SOURCE EFFLUENT GASES

| *Source* | *Conc. of aldehydes, as p.p.m. or μg/l* |
|---|---|
| range oven[6] | 11 p.p.m. |
| water heater[6], 100 gallon | 8 p.p.m. |
| floor furnace[6] | 3 p.p.m. |
| steam boiler[6], low fire | 5 p.p.m. |
| fuel gas combustion[1] | 60 μg/l |
| fuel oil combustion[1] | 75 μg/l |
| domestic incinerator-Timmings[1] | 125 μg/l |
| domestic incinerator-paper[1] | 44 μg/l |
| domestic incinerator-mixed change[7] | 180–1960 μg/l |
| municipal incinerator[1] | 60 μg/l |
| automobile exhaust – idle[1-3] | 100 μg/l, 88 p.p.m., 60 p.p.m. |
| – cruise[1-4] | 200 μg/l, 264 p.p.m., 140 p.p.m., 70–96 p.p.m. |
| – accel.[2] | 1369 p.p.m. |
| – decel.[2,3] | 193 p.p.m., 190 p.p.m. |
| diesel engine[5] | 7 p.p.m. |

The formaldehyde concentration in a multiple-chambered experimental incinerator was only in the 0.1 to 1 p.p.m. range when a high volatile fuel was used[8]. Formaldehyde was determined by direct sampling into sulfuric acid containing 0.1% chromotropic acid.

The formaldehyde content of auto exhaust was found to range from 29 to 43 p.p.m. for 15, 40 and 60 MPH cruise conditions[4]. The phenylhydrazine and potassium cyanide methods were used for analysis of the formaldehyde. The formaldehyde was just under half of the total aldehyde content in this investigation[4].

An analysis indicating 3 p.p.m. of acrolein in automobile exhaust has been reported[1]. No experimental details are available. Polarographic determinations of acrolein produced in mold pouring and varnish cooking operation[9] were reported as 0.5 and 0.4 p.p.m. The corresponding total aldehydes[9] (as formaldehyde) were reported to be 3.3 and 2.0 p.p.m.

This brief survey is not meant to represent an exhaustive review of the literature. The data does point out the relatively large emissions of aldehydes per unit of volume from automobiles and domestic incinerators. More exhaustive and specific analyses for total and individual aldehydes on some of the sources in Table I would be desirable.

## PREVIOUS EXPERIMENTAL RESULTS ON THE ATMOSPHERE

A considerable number of measurements of atmospheric "aldehyde" content by the bisulfite method have been reported[6,49–54]. Concentrations exceeding 1 p.p.m. have been reported, with a number of maximum values between 0.5 and 1 p.p.m. Average aldehyde values in the Los Angeles basin are in the 0.1 to 0.5 p.p.m. range[6]; however, average values in most localities are around 0.05 p.p.h.m.[49,50]. Many of the older data have been tabulated elsewhere[49].

Data also is available on three more recent studies in Houston[51] and El Paso, Texas[52] and in Southern Ontario[53]. In the Houston[51] study most of the concentrations were in the 0–0.1 p.p.m. range with one value of 0.3 and another of 1.3 p.p.m. In the El Paso[52] study a considerable number of daily measurements were made at three stations over two periods of several months each. The average aldehyde values (again by the bisulfite method) were around 0.05 p.p.m. However, maximum values between 0.4 and 0.5 p.p.m. were obtained. A more detailed analysis of the data shows that while most of the values were in the 0.00 to 0.05 range, 10 or 20% of the values are in the 0.1 to 0.2 p.p.m. range[52]. In the Southern Ontario studies it was reported that most of the readings were below 0.70 p.p.m. but that peaks as high as 3 p.p.m. were measured[53]. A study in the Southern Ontario[54] area 7 years before this work gave an average value of 0.2 p.p.m. and a maximum value of 0.75 p.p.m.

A small number of determinations of aldehydes as formaldehyde and separately of ketones have been made by polarographic reduction of the semicarbazones[15]. One measurement made on the Los Angeles atmosphere gave 0.6 p.p.m. aldehydes and 0.4 p.p.m. ketones as acetone. Later measurements on solutions several days old which may have lost their aldehyde content gave 0.1–0.2 p.p.m. as acetone[15].

With a few exceptions the number of atmospheric "aldehyde" measurements even by the bisulfite method at various localities is small. The measurements made thus far show that there are times in a number of cities during which the "aldehyde" content may reach 0.5 p.p.m. or higher. Such concentrations are comparable with the sulfur dioxide, nitric oxide, and hydrocarbon contents in many localities. Since the aldehydes have been related to many deletorious effects, more measurements of total carbonyls, total aldehydes, formaldehyde and unsaturated aldehydes in urban atmospheres are both desirable and necessary.

## EXPERIMENTAL RESULTS ON THE ANALYSIS OF FORMALDEHYDE IN AUTOMOBILE EXHAUST EFFLUENT

An investigation has been made in our laboratories of the applicability of various modifications of the chromotropic acid method to the analysis of formaldehyde in the automobile exhaust. The automobile was run on a 30 MPH cruise. The chromotropic acid method was chosen because of its good sensitivity and ease of application. Most of the sampling was done directly into evacuated 2-l glass flasks. Some samples were collected in aluminized scotchpak bags, others directly into impingers and bubblers.

No formaldehyde could be detected in exhaust gas samples collected into aluminized scotchpak bags, and then transferred to evacuated flasks containing 1% aqueous sodium bisulfite solutions. Essentially no formaldehyde could be determined in samples collected in evacuated flasks, bubblers or impingers containing 0.1% chromotropic acid in sulfuric acid. Finally, when the samples were collected in empty flasks to which 1% aqueous sodium bisulfite solution was added later, no formaldehyde could be recovered.

Appreciable amounts of formaldehyde can be determined in samples collected directly into evacuated flasks containing water, 1 or 40% bisulfite solutions or into

TABLE II

FORMALDEHYDE IN AUTOMOBILE EXHAUST AS DETERMINED BY VARIOUS CHROMOTROPIC ACID PROCEDURES

| *Collection solution* | *Reaction time outside flask, in min* | *Formaldehyde in p.p.m. Time period between sampling and removal of sample from flask, in min* | | | |
|---|---|---|---|---|---|
| | | *5* | *10* | *15* | *20* |
| water | <5 | 21 | 15 | <1 | <1 |
| water | 60 | 24 | 19 | <1 | <1 |
| 1% aqueous bisulfite | <5 | 21 | 15 | 10 | 6 |
| 40% aqueous bisulfite | <5 | 21 | 14 | 13 | 12 |
| 40% aqueous bisulfite | 60 | 27 | 27 | 26 | 25 |

TABLE III

FORMALDEHYDE IN AUTOMOBILE EXHAUST AS DETERMINED BY CHROMOTROPIC ACID METHOD AFTER COLLECTION IN 40% BISULFITE SOLUTION

| *Reaction time outside flask, in min* | *Formaldehyde in p.p.m. Time period between sampling and removal of sample from flask, in min* | | | |
|---|---|---|---|---|
| | *1* | *15* | *30* | *60* |
| 5 | 24 | 16 | 15 | 16 |
| 30 | 26 | 23 | 21 | 20 |
| 60 | 26 | 22 | 23 | 24 |
| 120 | 28 | 23 | 22 | 23 |

impingers containing the same solutions. Very small amounts of formaldehyde can be detected from samples passed through a bubbler containing 1% bisulfite solution. The samples passed through the impingers containing 1 or 40% bisulfite solution analyzed to give only 20 to 40% of the formaldehyde content found for equivalent samples collected in evacuated flasks containing the same solutions.

The results in p.p.m. by volume of formaldehyde under different collection and reaction conditions are shown in Tables II and III. These data indicate that it is desirable to remove the aliquot for analysis from the flask as rapidly as practical, and that a waiting period of about 1 h is desirable before chromotropic acid is added to the aqueous aliquot. If 40% bisulfite solution is used and the aliquot is held for as much as 1 h before analysis, only a 10 to 20% decrease in concentration will result even if the aliquot for analysis remains in the flask for 1 h.

Extrapolation of the present data to zero time in flask after collection, with a 60-min holding time before analysis, would result in a formaldehyde concentration of just under 30 p.p.m. In previous work an average formaldehyde concentration of 29 p.p.m. (range 25–33 p.p.m.) at 15 MPH cruise and 39 p.p.m. (range 28–51 p.p.m.) at 40 MPH cruise were reported. A concentration of about 30 p.p.m. at 30 MPH cruise certainly is in the same range. Considering the difference in fuels and operating conditions (engine dynamometer *versus* automobile on chassis dynamometer) the general agreement is very good.

The loss of formaldehyde found when sampling into a scotchpak bag can be explained without difficulty. Hot exhaust is being collected and as condensation of water occurs, formaldehyde is carried down with it. Any formaldehyde remaining may be lost by adsorption on the liquid film formed on the surface of the bag. The loss of formaldehyde in dry glass flasks further indicates the great difficulty of sampling into a dry container. It is much more difficult to understand the essentially complete loss in the glass flasks. It might be thought that losses on the walls would be recovered when the absorbing solution is added. However, these results were obtained on four different flask samples. In all of these runs the aliquot for analysis was removed less than 5 min after addition of the 1% bisulfite solution. Irreversible reactions of formaldehyde in the dry flask must remove it permanently from the gas and surface phases.

The inability to detect formaldehyde when sampling into flasks, bubblers or impingers containing 0.1% chromotropic acid in sulfuric acid must be attributed to loss of formaldehyde through reaction with interfering substances, particularly aromatic species. The lower formaldehyde concentrations found when sampling into bisulfite solutions in bubblers or impingers rather than evacuated flasks are somewhat more troublesome to explain. It may be that interfering materials are collected by the bubblers or impingers containing bisulfite solution more effectively than by the bisulfite solution in the flask. Support for this argument is found in the lower formaldehyde concentrations obtained even for samples collected in flasks, if the aliquot for analysis is not removed immediately. Apparently, the formaldehyde is collected quite rapidly and efficiently by the bisulfite solution in the flasks, but the interfering substances are absorbed by the aqueous bisulfite solution more slowly. The decrease in formaldehyde is not likely to be the result of polymerization or volatilization of formaldehyde. Samples removed from the flasks and allowed to stand in test tubes actually analyze to give higher formaldehyde concentrations than those analyzed immediately. The latter result may be due to hydrolysis of combined formaldehyde, since the aqueous solutions are acidic. Perhaps, part of the increase is due to the hydrolysis of formals produced in the combustion process. Some evidence for their existence is available from gas chromatographic studies of automobile exhaust from pure hydrocarbon combustion[18].

Acrolein has been found in automobile exhaust up to concentrations of 9 p.p.m., Table IV. The concentration found for a given automobile may be very sensitive to engine or carburetor adjustments. The same automobile which produced 7–9 p.p.m. during a number of runs produced only about 1 p.p.m. after carburetor adjustment. After a running of the same automobile a number of additional hours, the acrolein concentration climbed up to 4 p.p.m. It is possible that both formaldehyde and acrolein are very sensitive indices of minor changes in automobile operating conditions.

TABLE IV

ANALYSES FOR ACROLEIN IN AUTOMOBILE EXHAUST

| *Type of sample* | *Collection method* | *Conc. of acrolein, p.p.m. by volume* |
|---|---|---|
| cruise auto exhaust[a] | bubblers | 8.3 |
| cruise auto exhaust[a] | plastic bag[b] | 8.7 |
| decel. (coasting) exhaust | plastic bag[b] | 7.0 |
| cruise and decel. exhaust | bubblers | 7.0 |

[a] 30 MPH cruise samples collected at about the same time
[b] aluminized scotchpak bag

## ANALYSIS OF DILUTED AUTOMOBILE EXHAUST

A number of analyses of the formaldehyde concentration were made after dilution but before irradiation. Samples were collected directly into impingers or bubblers from a tap in the dilute exhaust line going into an irradiation chamber. Impingers were used for collecting the formaldehyde in 0.1% chromotropic acid in sulfuric acid[35], while bubblers were used when collecting samples in water[34,35] or 2-hydrazino-benzothiazole reagent[38].

Typical results for formaldehyde using the three collecting solutions were as follows: (*1*) 0.1% chromotropic acid in sulfuric acid, 8 p.p.h.m.; (*2*) 0.25% aqueous 2-hydrazinobenzothiazole solution, 46 p.p.h.m.; (*3*) water, 60 p.p.h.m. Again, as found for exhaust directly from the engine, collection of diluted exhaust in sulfuric acid gave extremely low results for the formaldehyde.

Some preliminary results on formaldehyde were made on even more highly diluted automobile exhaust by collection in sulfuric acid containing 0.1% chromotropic acid. Comparison of the formaldehyde contents obtained by this procedure with those obtained by collection in aqueous solutions indicates more satisfactory results in the more diluted gas mixture. However, direct collection of automobile exhaust gases in sulfuric acid medium usually gave quite unsatisfactory results and should be avoided.

Higher formaldehyde values are found by analyzing with chromotropic acid reagent after collection of the formaldehyde in aqueous media than when analysis is made subsequent to collection in 2-hydrazinobenzothiazole reagent. The difference observed could be due to interferences or to the two methods measuring different species.

Both alternatives are possibilities. However, all of the experimental data available on the chromotropic acid method indicate that almost all of the possible major interferences tend to reduce the measured formaldehyde content. No significant interferences have been reported for the 2-hydrazinobenzothiazole method[38]. In both methods some higher aldehydes and diketones give a small response which might increase the observed absorbance, but by only a few percent at most. The other alternative is that the chromotropic acid procedure is measuring formaldehyde and also a significant quantity of formals while the 2-hydrazinobenzothiazole only measures formaldehyde. Some evidence for such a possibility has been discussed in the previous section. Further investigation will be necessary to interpret these differences with any certainty.

Acrolein has been determined on the same runs for which formaldehyde data are available[42]. The acrolein concentration in the diluted non-irradiated automobile exhaust was in the 4 to 6 p.p.h.m. range. Consequently, the acrolein concentration was about 10% of the formaldehyde concentration.

## ANALYSIS OF DILUTED, IRRADIATED AUTOMOBILE EXHAUST

A larger number of analyses have been made on irradiated exhaust for formaldehyde and acrolein. Most of the determinations for formaldehyde have been made by various of the chromotropic acid procedures[34,35]. However, a number of determinations have been made using both collection into sulfuric acid, water or bisulfite solution with the chromotropic acid method and collection in 2-hydrazinobenzothiazole reagent[38].

Most of determinations were made on samples pulled out of a mylar bag filled with the irradiated exhaust. Formaldehyde diluted in air was moderately stable in a mylar bag. The following absorbances were obtained when 5-l samples were analyzed by the chromotropic acid method after the formaldehyde had remained in the bag for some time: 0.5 h, 0.88; 2.5 h, 0.89; 20.5 h, 0.87; 24 h, 0.84. However, actual irradiated exhaust samples lost formaldehyde from the gas phase somewhat rapidly. Two different runs showed that a 5 to 10% loss of formaldehyde occurred (probably to the walls) after the sample remained in the bag for about 2 h.

This loss would not invalidate the main results obtained in the comparative determinations. Furthermore, the duplicate determinations by one of the procedures made in two of the runs allow corrections to be made for the losses experienced. In addition to the bag runs, several determinations were made at the same or nearly the same times on samples taken into bubblers directly from the irradiation chamber.

TABLE V

FORMALDEHYDE ANALYSIS ON DILUTED, IRRADIATED EXHAUST

| *Run* | *Analytical method* | *Collection medium*[a] | *Formaldehyde conc. p.p.m. by volume* |
|---|---|---|---|
| 1 | chromotropic acid | water | 2.7[b] |
| | 2-hydrazinobenzothiazole | 0.25% aq. 2-HTB | 2.1 |
| | chromotropic acid | water | 2.5 |
| | chromotropic acid | 0.1% chromotropic acid in $H_2SO_4$ | 1.7 |
| 2 | chromotropic acid | 0.1% chromotropic acid in $H_2SO_4$ | 2.1 |
| | 2-hydrazinobenzothiazole | 0.25% aq. 2-HTB | 2.3 |
| | chromotropic acid | water | 2.5 |
| 3 | chromotropic acid | water | 2.5 |
| | 2-hydrazinobenzothiazole | 0.25% aq. 2-HTB | 2.1 |
| 4 | chromotropic acid | 0.1% chromotropic acid in $H_2SO_4$ | 2.3 |
| | 2-hydrazinobenzothiazole | 0.25% aq. 2-HTB | 2.6 |
| | chromotropic acid | water | 3.1 |

[a] Samples of raw exhaust, diluted 100 : 1 and irradiated were pulled out of irradiation chamber into a mylar bag and then pulled through the collecting medium contained in a bubbler or impinger.

[b] Four formaldehyde analyses by this procedure on samples collected in bubblers directly from chamber averaged 2.9 ± 0.2 ($\sigma$) p.p.m.

Four sets of determinations on a mylar bag sample are shown in Table V. The determinations from all of the runs were averaged and the analyses obtained by the 2-hydrazinobenzothiazole proved to give 0.85 of the formaldehyde concentration obtained by sampling into water or bisulfite solution and then reacting with chromotropic acid reagent. The direct sampling and analysis with 0.1% chromotropic acid reagent in sulfuric acid gave 0.75 of the formaldehyde concentration obtained by sampling into water or bisulfite solution and then reacting with chromotropic acid reagent. Consequently, the very simple and sensitive procedure of directly sampling and analyzing in 0.1% chromotropic acid in sulfuric acid may be applicable in atmospheric analysis work. It should be mentioned that the fuels used contained 40% aromatic hydrocarbons. Thus the interference situation in the irradiated system used actually may be worse than in the atmosphere for this chromotropic acid procedure[35]. The previous discussions probably apply to the lower results obtained for formaldehyde content by the 2-hydrazinobenzothiazole method compared to the aqueous sampling procedure with the chromotropic method on the irradiated samples. However, little is known about the interference problems in the 2-hydrazinobenzothiazole method in the very complicated diluted, irradiated automobile exhaust systems.

Acrolein determinations were made on the same runs[42]. While the formaldehyde determinations using aqueous collecting medium and the chromotropic acid method averaged 2.7 p.p.m., the acrolein concentration for the same runs averaged 0.18 p.p.m.

The formaldehyde found in the exhaust diluted 100 : 1, 0.6 p.p.m., is about 22% of the formaldehyde found in the corresponding irradiated exhaust. The acrolein in the diluted, non-irradiated exhaust constitutes about one-third of the acrolein found in the irradiated exhaust. Consequently, most of these two aldehydes are produced by photooxidation reactions, but the contribution directly from the automobile is significant. These results should be generalized with caution. The data is obtained by burning special experimental gasolines in a single automobile mounted on a chassis dynamometer, diluting the exhaust with purified air, and irradiating the mixture in an aluminium chamber with fluorescent lamps through mylar windows[55].

## CONCLUSION

The previous discussion indicates that there are available many potential methods for the analysis of aldehydes in combustion sources and in the atmosphere. Several of the volumetric and colorimetric methods have been applied successfully to air pollution situations. More colorimetric methods for certain aldehyde subclasses would be desirable. Polarographic procedures, perhaps along with other electrometric methods, appear to have a certain real range of applicability. Gas chromatography can be applied to many somewhat simplified systems. Better column materials and detectors should increase the applicability of gas chromatography to aldehyde analysis. Infrared and mass spectrometric methods have some applicability in aldehyde analysis in simple laboratory systems. However, they are much more powerful tools when applied in combination with other methods.

Of the methods discussed, a few of the volumetric techniques and a number of the colorimetric procedures for aldehydes have real applicability to rapid analysis of many samples in the field or laboratory. The others, with the possible exception of some polarographic or electrometric techniques, are essentially research methods. These methods alone or in combination can provide a great deal of valuable detailed information on a few samples, at a rather high cost in personnel and equipment per sample.

The chromotropic acid method employing collection in aqueous solution is the simplest, most rapid and generally convenient procedure for analysis of raw, diluted and irradiated automobile exhaust and numerous other applications. The hydrazinobenzothiazole method is much more time-consuming, and the sensitivity is less than twice that of the chromotropic acid procedure. Direct collection in 0.1% chromotropic acid in sulfuric acid provides an extremely rapid and simple procedure. Since no dilution is involved, the method is considerably more sensitive than the hydrazinobenzothiazole method. However, the procedure is not applicable to some types of combustion source analysis. Direct collection in chromotropic acid does appear usable for atmospheric or irradiation chamber analysis.

The 4-hexylresorcinol method is highly sensitive. It is applicable to the analysis of raw, diluted and irradiated automobile exhaust and other gases and liquid phase analysis for acrolein.

Despite some limitations in our analytical methodology, we have many methods available which have rarely, if ever, been applied to the analysis of aldehydes in air pollution situations. Much more information can and should be obtained with existing techniques on all types of combustion and pyrolysis source samples and on urban atmospheres. Meanwhile continued research effort should provide us with new methods which will fill the gaps in our existing arsenal of analytical procedures for aldehydes.

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# DONNÉES RELATIVES AUX ÉQUILIBRES CHIMIQUES RÉGISSANT LA SÉPARATION ZIRCONIUM-HAFNIUM

## IIème et IIIème parties*

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(Reçu le 21 novembre, 1960)

## II. LA TROISIÈME PHASE

Nous avons vu dans la première partie, l'importance du phénomène d'apparition d'une 3ème phase, lorsqu'on extrait des solutions concentrées de zirconium par un faible volume de solvant; on voit alors la phase solvant se partager en deux: (*a*) une phase riche en tributylphosphate et en zirconium, (*b*) une phase riche en diluant.

Ce phénomène est gênant dans une installation de production, en ce qu'il oblige à travailler avec des débits de solvants supérieurs à ce qui est nécessaire au simple point de vue du rendement. Nous avons donc été amenés à étudier de près ce problème, à la suite de HUDSWELL *et al.*[1], qui avaient déjà examiné quelques facteurs: rôle du diluant, de la température et de la concentration de la solution aqueuse en acide nitrique et zirconium. Leur travail, très intéressant, était un travail de dégrossissage destiné plutôt à la sélection du diluant. Ces auteurs ont noté en particulier qu'en présence de xylène on n'a jamais trois phases. Un point important, sur lequel HUDSWELL ne donne pas de précisions, est la concentration maximum en zirconium de la phase organique au-delà de laquelle on obtient une démixtion du solvant. Nous avons étudié la variation de cette concentration limite en fonction de divers facteurs qui nous ont semblé devoir jouer un rôle.

Nous examinerons: (1) l'influence de la température, (2) l'influence du % de tributylphosphate dans le solvant, (3) l'influence de l'acidité de la phase aqueuse de départ, (4) l'influence du diluant, (5) l'influence des produits de décomposition du tributylphosphate (cas du dibutylphosphate), (6) l'influence d'une addition d'aromatique (xylène) au diluant.

*Nota.* Nous savons que l'hexane utilisé comme diluant, se comporte comme la xylène et ne donne jamais de 3ème phase. C'est un solvant dont l'utilisation industrielle paraît interessante à un autre point de vue: sa faible densité (0.66) et sa faible viscosité (0.32 c.p.) permettent une séparation rapide des phases aqueuse et organique, et par conséquent, des débits plus importants que tout autre diluant, dans une installation industrielle donnée. PHILOON *et al.*[2] décrivent une installation pour la production d'uranium utilisant l'hexane. Malheureusement, sa grande volatilité et son bas point éclair imposent des précautions irréalisables dans l'état actuel de l'atelier de production français, et nous l'avons pour cette raison, exclu de notre étude.

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* Ire Partie: *Anal. Chim. Acta*, 25 (1961) 1.

## MODE OPÉRATOIRE

On verse dans une ampoule à décanter successivement 50 ou 60 ml de tributylphosphate, 50 ou 40 ml de diluant, 50 ml d'eau, 50 ml d'acide nitrique concentré (10 ou 12 *N*). Après agitation, décantation et filtration, on obtient environ 100 ml de solvant acide. Nous disposons par ailleurs d'une solution de zirconium dont l'acidité libre (pour la définition de l'acidité, *cf.* la Ière partie de ce rapport) sera ajustée à 5 ou 6 *N* selon les besoins. À 5 ou 10 ml de solution zirconium, on ajoute, à la burette ou à la pipette, un volume $x$ de solvant et on équilibre les phases, par agitation et décantation, dans un thermostat réglé à la température désirée. On ajoute ainsi du solvant jusqu'à ce que la 3ème phase disparaisse. Le zirconium est alors dosé dans la phase solvant.

## RÉSULTATS

### *I. Influence de la température, de la concentration du solvant en tributylphosphate et de l'acidité de la phase aqueuse initiale, sur la concentration limite de zirconium dans une phase solvant homogène*

Le diluant est du white spirit "Lavera" soit un mélange de paraffines droites ($d = 0.75$; $130° < E < 190°$).

TABLEAU I

CONCENTRATION EN ZIRCONIUM DANS LA PHASE SOLVANT À LA LIMITE D'APPARITION DE LA 3ÈME PHASE

| *Solvant 50–50* | *6 N* | *5 N* | *Solvant 60–40* | *6 N* | *5 N* |
|---|---|---|---|---|---|
| 20° | 14.5 g/l | 14.7 g/l | 20° | 22.0 g/l | ⩽22.5 g/l |
| 30° | 17.8 g/l | 17.8 g/l | 30° | ⩽26.5 g/l | 26.7 g/l |

Ces résultats permettent de dégager nettement l'influence des divers facteurs: (*1*) Importance du coefficient de température*, (*2*) Influence faible ou nulle de l'acidité de la phase aqueuse (dans les limites expérimentales décrites), (*3*) Importance de la concentration en tributylphosphate du solvant: en effet, à une diminution de 1/6 de la teneur en tributylphosphate du solvant, correspond une diminution de: $7.4/22 \simeq 1/3$ de la teneur limite en zirconium.

### *II. Influence du diluant*

En utilisant la même technique, nous avons essayé de comparer le pouvoir solvant de différents diluants. Les diluants essayés ont été: le white spirit "Lavera", le dodécane, le white spirit fourni par la Société des Hydrocarbures de Saint-Denis, dont on sait seulement qu'il contient moins de 5% d'aromatique. À chacun de ces diluants, nous avons ajouté des proportions croissantes de xylène. Le Tableau II nous donne la teneur limite de la phase solvant à 20° en fonction du % xylène dans le mélange tributylphosphate + diluant + xylène (*cf.* aussi Fig. 1).

La précision des résultats est de ± 3%. Ces résultats semblent montrer que le

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* Nous avons vérifié que la température dans le domaine considéré était sans influence sur le coefficient de partage du zirconium.

TABLEAU II

| *Diluant* | *% xylène* | *0* | *5* | *10* | | | | |
|---|---|---|---|---|---|---|---|---|
| "Lavera" | Zr g/l $\varphi_s$ | 14.6 | 20.0 | 26.8 | | | | |
| Dodécane | % xylène | 0 | 2 | 5 | 7 | 10 | 15 | 20 |
| | Zr g/l $\varphi_s$ | 20.7 | 22.7 | 25.1 | 26.7 | 29.7 | 35.3 | 42.5 |
| St. Denis | % xylène | 0 | 2.5 | 5 | 10 | 20 | | |
| | Zr g/l $\varphi_s$ | 22.7 | 23.8 | 26.5 | 31 | 44.7 | | |

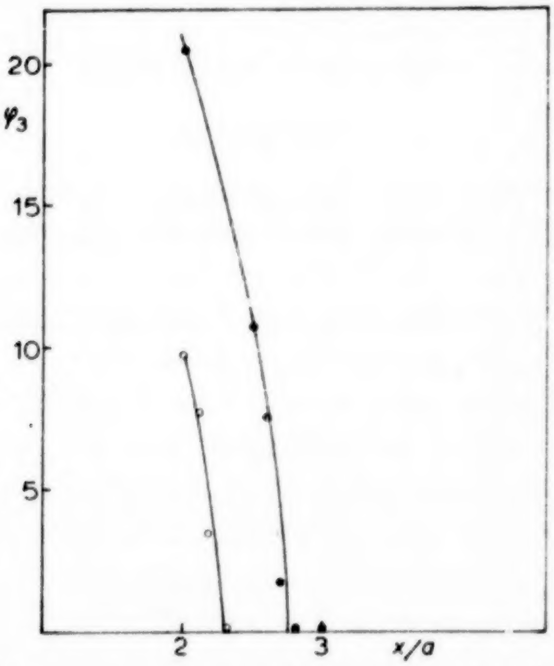

Fig. 1. Importance de la 3ème phase en fonction des rapports de volume solvant/phase aqueuse. ● 2% DBP; ○ 6% DBP.

white spirit des hydrocarbures de Saint-Denis correspond bien — ou équivaut — à un dodécane contenant environ 4% de xylène.

### *III. Influence des produits de dégradation du tributylphosphate: le dibutylphosphate*

Le mode opératoire reste le même: on mélange dans l'ampoule à décanter 50 ml de tributylphosphate, (50 — *n*) ml de white spirit Saint-Denis, *n* ml de dibutylphosphate, 50 ml d'acide nitrique concentré et 50 ml d'eau; on agite et décante (une logique rigoureuse aurait exigé que le dibutylphosphate fût mis en remplacement du phosphate de tributyle et non du diluant, mais les résultats ne seraient pas exactement comparables aux précédents). Le solvant ainsi préparé sera utilisé, à 20°, suivant la même technique que précédemment: addition à 10 ml de solution aqueuse de zirconium d'une quantité croissante de solvant jusqu'à disparition de la 3ème phase.

Nous avons cette fois noté le volume de la 3ème phase $\varphi_3$, le volume total de solvant, $x$, et le volume de phase aqueuse, $a$, et porté sur le tableau les valeurs de $\varphi_3/x$ en fonction de $x/a$. Ceci donne une idée de la précision avec laquelle on détermine le point de disparition de la 3ème phase (*cf.* Tableau III et Fig. 2).

Sachant que pour le solvant initial, sans dibutylphosphate ($< 0.1$ %), la teneur limite pour le zirconium est 22.8 g/l, on constate que, au moins pour les teneurs qui nous intéressent, la concentration limite en zirconium du solvant augmente pro-

TABLEAU III

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2% DBP | $\frac{x}{a} = \frac{vol\,\varphi_s}{vol\,\varphi_a}$ | 2 | 2.5 | 2.6 | 2.7 | 2.8 | 3 | $x/a = 2.8 \rightarrow \mathrm{Zr}\,\varphi_s = 27$ g/l |
| | $\varphi_3/x$ | 0.20 | 0.11 | 0.075 | 0.017 | 0 | 0 | |
| 5.92% DBP | $x/a$ | 2 | 2.1 | 2.2 | 2.3 | 2.5 | | $x/a = 2.3 \rightarrow \mathrm{Zr}\,\varphi_s = 34$ g/l |
| | % $\varphi_3/x$ | 0.097 | 0.077 | 0.034 | 0 | 0 | | |

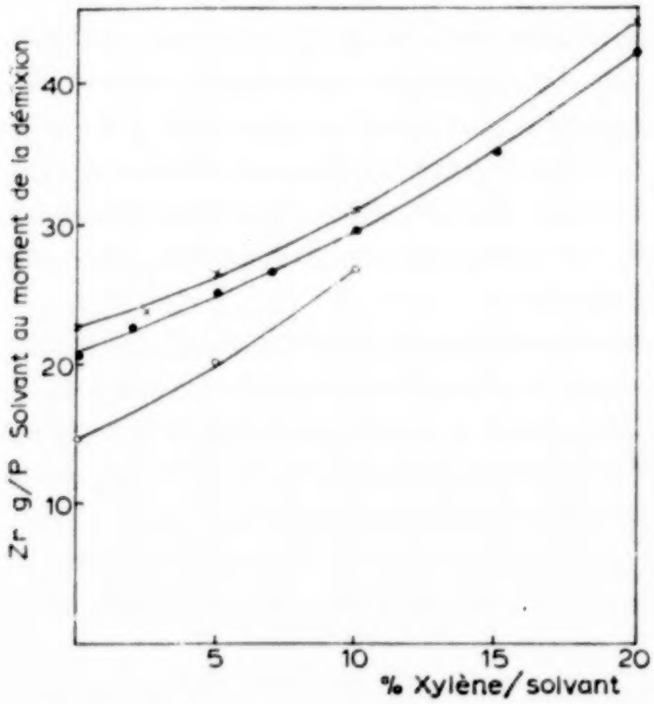

Fig. 2. Teneur limite du solvant en zirconium en fonction de la quantité de xylène présente. Diluants, ○ "white spirit" Lavera; ● dodécane; × "white spirit" St. Denis.

portionnellement à la teneur en dibutylphosphate et ce, de 2.2 g Zr/l/% de dibutylphosphate. L'influence du dibutylphosphate est donc loin d'être négligeable.

## *IV. Application pratique: évolution du solvant utilisé pour la production*

On constate au fur et à mesure du "vieillissement" du solvant que la concentration limite admissible pour le zirconium augmente au cours du temps. Nous avons pu montrer que ce phénomène était dû à deux causes:

(*1*) augmentation de la teneur en dibutylphosphate par hydrolyse du solvant, teneur qui est passée de 0.1 à 0.6%.

(*2*) augmentation de la teneur en tributylphosphate par évaporation du diluant plus volatil: la concentration en tributylphosphate est passée de 50 à 58%. Malheureusement, cette caractéristique n'est pas intéressante pour la production; en effet, l'augmentation de la concentration en dibutylphosphate est génératrice d'émulsions et augmente la rétention du zirconium dans le solvant; l'augmentation de la concentration en tributylphosphate, en augmentant la viscosité du mélange, ralentit la décantation et limite ainsi les débits de liquide admissibles. Une addition d'aromatiques paraît plus utile si l'on veut accroître la capacité en zirconium du solvant: il devient, en effet, possible d'augmenter la production en gardant un débit total de liquide constant; ce débit total étant évidemment le débit maximum compatible avec un bon fonctionnement des extracteurs.

## III. LE VIEILLISSEMENT DU SOLVANT

Nous allons examiner rapidement les effets occasionnés par ce qu'on appelle le "vieillissement" du solvant. Au fur et à mesure des recyclages on constate:

(*a*) une élévation continue du taux d'extraction du zirconium, que semble accompagner une augmentation de l'extraction du hafnium, d'où production d'une zircone mal déhafniée;

(*b*) une rétention croissante du zirconium dans le solvant: le lavage à l'eau ne récupère qu'une fraction du zirconium réellement extrait. Cette fraction récupérée est d'autant plus faible que le zirconium a séjourné plus longtemps dans le solvant;

(*c*) un solvant qu'on a laissé ainsi vieillir, pendant un mois par exemple, en présence de zirconium, devient parfaitement inutilisable même s'il était encore convenable au moment de son stockage: on a, à la fois, des émulsions et des résultats défectueux pour la déhafniation.

On connaît par ailleurs les différents produits de dégradation du tributylphosphate: mono et dibutylphosphate, acide phosphorique et butanol. Enfin, certaines études récentes ont montré[3] que, dans le traitement des combustibles irradiés, la présence de très faibles quantités de dibutylphosphate (DBP) était responsable de la mauvaise décontamination de l'uranium, surtout en $^{95}$Zr.

Notre étude a porté sur la formation du dibutylphosphate au cours du temps et son influence sur l'extraction et la réextraction du zirconium en quantités pondérales.

### MODE OPÉRATOIRE

### *A. Préparation des solutions*

Une solution aqueuse de zirconium hafnié contenant 6 moles/l d'acide nitrique libre est notre solution mère. Elle sera ajustée suivant les besoins avec $HNO_3$ 6 *N*. Le solvant est un mélange en volume, de 60% de tributylphosphate et 40% d'un diluant: white spirit, xylène au hexane. Ce solvant est, avant usage, agité avec un égal volume d'acide nitrique 6 *N*. On extrait avec un volume de solvant acide un égal volume de solution nitrique de zirconium de concentration égale respectivement à 3 et 30 g Zr/l.

Nous avons ainsi préparé 4 solvants chargés en zirconium: (*A*) tributylphosphate–white spirit contenant 2.7 g/l Zr, (*B*) tributylphosphate–white spirit contenant 19.7 g/l Zr, (*C*) tributylphosphate–xylène contenant 19.7 g/l Zr, (*D*) tributylphosphate–hexane contenant 19.3 g/l Zr.

Chacune de ces solutions représente 1 l de solvant environ. Des aliquotes sont prélevées régulièrement pour suivre la teneur en dibutylphosphate; simultanément on a récupéré par un lavage à l'eau le zirconium qu'elles contenaient.

Lorsque le solvant est frais, la totalité du zirconium (plus de 98%) est récupérée par lavage d'un volume de solvant par un égal volume d'eau; lorsque le solvant a vieilli, l'eau du premier lavage ne contient qu'une partie du zirconium initialement présent dans le solvant. On a vérifié que le zirconium ne passe, dans un second lavage, que dans des proportions très faibles ($< 3\%$).

### *B. Méthodes analytiques: dosage du dibutylphosphate*

Cette méthode est une modification de celle mise au point par la SOCIÉTÉ SAINT-GOBAIN[4]. On utilise le fait que le sel de sodium du dibutylphosphate (DBP Na) est soluble dans l'eau et peu soluble dans les solvants organiques, ce qui permet de le séparer du tributylphosphate.

Par acidification de la phase aqueuse on reforme le dibutylphosphate acide (DBP H) soluble dans les solvants organiques et peu soluble dans l'eau. Une extraction par le benzène sépare donc DBP H des acides minéraux non extractibles; il suffit ensuite de doser par acidimétrie la phase benzénique.

On élimine la majeure partie du zirconium contenu dans le solvant en lavant celui-ci avec $H_2SO_4$ 2 *N*. Puis on extrait le dibutylphosphate par un mélange de phosphate disodique et de fluorure de sodium (le fluorure en complexant le zirconium restant évite les émulsions possibles par formation de phosphate de zirconium) additionné de $Na_2CO_3$ pour donner un pH $\simeq$ 9; deux lavages du solvant suffisent (1 volume de solvant + 1/2 volume d'une solution à 20 g/l $Na_2HPO_4$ + 30 g/l NaF). On acidifie ensuite la phase aqueuse obtenue par HCl concentré et on extrait par deux fois avec 1/2 volume de benzène; la phase benzénique est lavée avec un volume d'HCl 0.1 *N* puis titrée par NaOH 0.1 *N*. Au cours de ces différentes extractions qui ne sont pas absolument quantitatives, le dibutylphosphate est récupéré dans la proportion de 96 %, ce qui introduit un facteur correctif dans les calculs.

Si $n$ est le volume en ml de NaOH *N*/10 versés, et $v$ le volume de la prise d'essai, on a: DPB % $= n/v$ 2.18.

Cette méthode permet de doser 20 à 200 mg de dibutylphosphate à ± 5 mg près environ.

## RÉSULTATS

Les résultats sont reproduits sur les Tableaux IV, V, VI, VII, et les Figs. 3 et 4. Nous appelons rétention % le rapport:

$$\frac{\textit{Zr restant dans le solvant après lavage}}{\textit{Zr initialement présent}}$$

TABLEAU IV

SOLUTION B

Diluant: white spirit; Zr/solvant: 19.7 g/l soit 0.216 mole/l; Date: 13.11.1958

| *Nombre de jours* | *Zr mg/ml récupéré* | *Rétention %* | *‰ DBP* | *DBP mole/l · $10^2$* | *DBP/Zr mole/mole* |
|---|---|---|---|---|---|
| 1 | 19 | 3.5 | 1.0 | 0.48 | 0.022 |
| 2 | 18.6 | 5.5 | 2.0 | 0.95 | 0.044 |
| 5 | 17.4 | 11.5 | 5.7 | 2.72 | 0.12 |
| 7 | 16.7 | 15 | 7.7 | 3.66 | 0.17 |
| 11 |  | 16 | 8.3 | 3.96 | 0.18 |
| 15 | 14.2 | 28 | 15.0 | 7.15 | 0.33 |
| 21 | 12.7 | 35.5 | 19.2 | 9.15 | 0.42 |
| 29 | 11.8 | 40 | 21.6 | 10.3 | 0.47 |
| 39 | 9.6 | 53 |  |  |  |
| 54 | 9.0 | 55 | 25.7 | 12.2 | 0.56 |
| 66 | 7.5 | 62 | 46 | 21.9 | 1.01 |

## TABLEAU V

### SOLUTION A

Diluant: white spirit; Zr/solvant: 2.7 g/l = 0.030 mole/l; Date: 13.11.1958

| *Nombre de jours* | *Zr mg/ml récupéré* | *Rétention %* | *‰ DBP* | *DBP mole/l · 10²* | *DBP/Zr mole/mole* |
|---|---|---|---|---|---|
| 3 | 2.43 | 11.5 | 0.5 | 0.24 | 0.08 |
| 9 | 2.18 | 19 | 1.18 | 0.56 | 0.18 |
| 11 | 2.17 | 20 | 1.68 | 0.80 | 0.26 |
| 15 | 1.97 | 26 | 2.30 | 1.10 | 0.36 |
| 18 | 1.84 | 32 | 2.7 | 1.28 | 0.40 |
| 25 | 1.55 | 42.5 | 3.2 | 1.52 | 0.50 |
| 31 | 1.42 | 47.5 | 3.7 | 1.76 | 0.58 |
| 39 | 1.32 | 51.5 | 4.4 | 2.70 | 0.70 |
| 64 | 0.84 | 69 | 6.7 | 3.18 | 1.06 |
| 72 | 0.70 | 74 | | | |

## TABLEAU VI

### SOLUTION D

Diluant: hexane; Zr/solvant: 19.3 g/l soit 0.212 mol/l; Date: 3.11.1958

| *Nombre de jours* | *Zr mg/ml récupéré* | *Rétention %* | *‰ DBP* | *DBP mole/l · 10²* | *DBP/Zr mole/mole* |
|---|---|---|---|---|---|
| 3 | 18.3 | 5 | 3.5 | 1.69 | 0.08 |
| 9 | 16.6 | 14 | 9.3 | 4.43 | 0.21 |
| 12 | 16.1 | 16.5 | 11.7 calc. | 5.56 | 0.27 |
| 15 | | | 14.2 | 6.75 | 0.32 |
| 16 | 15.2 | 21 | 15.2 calc. | 7.25 | 0.34 |
| 18 | 14.9 | 23 | 17.4 | 8.30 | 0.39 |
| 25 | 14 | 27.5 | 24.0 | 11.4 | 0.54 |
| 31 | 12.4 | 36 | 27.0 | 12.7 | 0.60 |
| 39 | 12 | 38 | 29.0 | 13.8 | 0.65 |
| 72 | 8.3 | 57 | 59 | 28.1 | 1.33 |

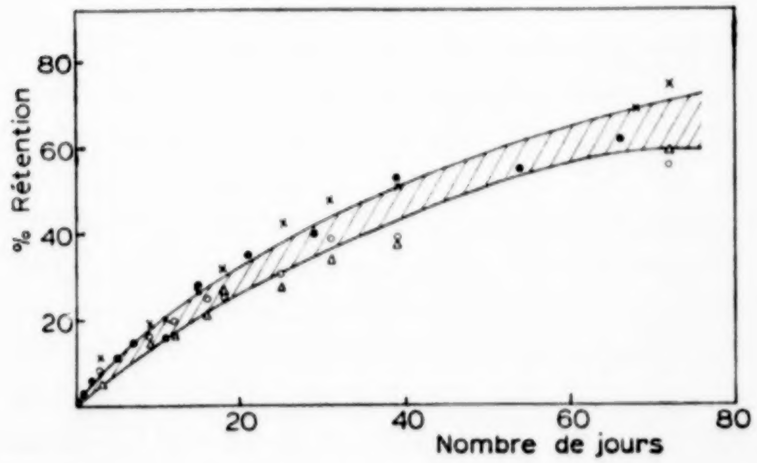

Fig. 3. Rétention du zirconium par le solvant en fonction du temps. ×, Solution A; ● Solution B; △ Solution C; ○ Solution D.

TABLEAU VII

SOLUTION C

Diluant: xylène; Zr/solvant: 19.7 g/l soit 0.216 mol/l; Date: 3.11.1958

| *Nombre de jours* | *Zr mg/ml récupéré* | *Rétention %* | *‰ DBP* | *DBP mole/l · 10²* | *DBP/Zr mole/mole* |
|---|---|---|---|---|---|
| 3 | 18.1 | 8 | 2.86 | 1.36 | 0.06 |
| 9 | 16.6 | 16.8 | 7.05 | 3.36 | 0.15 |
| 11 | | | 8.2 | 3.90 | 0.18 |
| 12 | 15.7 | 20 | 9.5 calc. | 4.53 | 0.21 |
| 15 | | | 12.3 | 5.86 | 0.27 |
| 16 | 14.8 | 25 | 13.0 calc. | 6.20 | 0.28 |
| 18 | 14.5 | 26.5 | 14.0 | 6.66 | 0.31 |
| 25 | 13.8 | 30 | 18.2 | 8.76 | 0.40 |
| 31 | 12.0 | 39 | 20.2 | 9.63 | 0.44 |
| 39 | 12.0 | 39 | 25.5 | 12.1 | 0.56 |
| 72 | 8.7 | 56 | 42 calc. | 19.5 | 0.90 |
| 76 | | | 44 | | |

Le ‰ de DBP représente un poids de dibutylphosphate par litre de solvant (tributylphosphate et diluant). Sur la Fig. 3 on voit que la rétention ne dépend pas du diluant. La dispersion des points est raisonnable si l'on tient compte du fait que les diluants ont des volatilités différentes et que les solutions ont pu se concentrer par évaporation au cours des 3 mois de stockage. Les courbes Fig. 4 montrent que la formation du phosphate dibutylique dépend en premier lieu de la quantité de zirconium présente dans le solvant. La quantité de dibutylphosphate formée semble

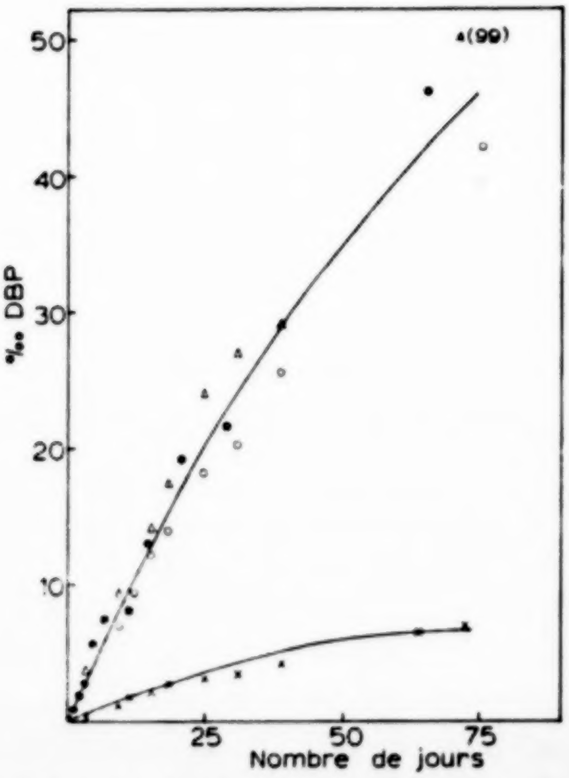

Fig. 4. Formation du DBP en fonction du temps. ○ Solution C; △ Solution D; ● Solution B; × Solution A.

tendre vers une limite, qui correspond probablement au "bloquage" de la totalité du zirconium présent dans le solvant.

Il existe incontestablement une relation entre la formation du dibutylphosphate et la rétention du solvant. Il nous reste à montrer que le dibutylphosphate est bien seul responsable du phénomène de rétention.

### ESSAIS SYNTHÉTIQUES

Ces essais ont été effectuées de deux manières différentes:

(*a*) la première consistait à ajouter du dibutylphosphate à un solvant frais contenant du zirconium et à étudier la réextraction et la rétention;

(*b*) la seconde consistait à ajouter le dibutylphosphate à un solvant non chargé ce qui permettait d'étudier simultanément l'extraction et la réextraction.

Les deux méthodes ont donné les mêmes résultats, ce qui montre que les équilibres sont rapides. Les Tableaux VIII, IX et X contiennent une partie des chiffres obtenus respectivement avec les diluants: white spirit, hexane. La Fig. 5 traduit la concordance des essais synthétiques et des expériences de vieillissement. Enfin, la Fig. 6 montre bien l'effet du dibutylphosphate sur l'extraction du zirconium.

TABLEAU VIII

ÉTUDE DE LA RÉTENTION DE Zr PAR LE DBP

Diluant, white spirit; Zr dans la solution aqueuse initiale: 30.2 g/l

| *‰ DBP* | *Zr g/l solvant* | *Extraction %* | *Rétention %* | *DBP/Zr mole/mole* |
|---|---|---|---|---|
| 0.0 | 19.5 | 65 | 0 | 0 |
| 0.97 | 19.6 | 65 | 1.5 | 0.021 |
| 4.8 | 20.2 | 67 | 8.0 | 0.10 |
| 9.7 | 20.8 | 69 | 13 | 0.20 |
| 19.2 | 23.1 | 76 | 28 | 0.36 |
| 35.0[a] | 19.5 | | 57.5 | 0.78 |
| 49.0[a] | 19.2 | | 74.5 | 1.12 |
| 70.3[a] | 18.7 | | 94 | 1.63 |

[a] Solutions obtenues par addition de DBP à un solvant contenant 20 g/l Zr

TABLEAU IX

Diluant, white spirit; Zr dans la solution aqueuse initiale: 3.00 g/l

| *‰ DBP* | *Zr g/l solvant* | *Extraction %* | *Rétention %* | *DBP mole/l · 10³* | *DBP/Zr mole/mole* |
|---|---|---|---|---|---|
| 0.45 | 2.65 | 86.5 | 8.5 | 0.214 | 0.074 |
| 0.9 | 2.73 | 89.5 | 15 | 0.427 | 0.14 |
| 1.8 | 2.77 | 91 | 22 | 0.854 | 0.28 |
| 3.6 | 2.85 | 93.5 | 41.5 | 1.71 | 0.55 |
| 4.5 | 2.88 | 94.5 | 54.5 | 2.14 | 0.67 |
| 9.0 | 2.98 | 97.5 | 85 | 4.27 | 1.29 |
| 18 | 3.05 | 100 | 100 | 8.54 | 2.58 |
| 45 | 3.05 | 100 | 100 | 17.5 | 5.47 |

### TABLEAU X

luant, hexane; solution, solvant contenant Zr auquel on ajoute du DBP

| *°/₀₀ DBP* | *Zr g/l solvant* | *Zr g/l récupéré* | *Rétention %* | *DBP/Zr mole/mole* |
|---|---|---|---|---|
| 12.9 | 19.7 | 15.3 | 23 | 0.28 |
| 34.2 | 19.5 | 8.2 | 57.6 | 0.76 |
| 42.4 | 19.4 | 6.3 | 68 | 0.94 |
| 52.8 | 19.3 | 4.5 | 76.7 | 1.19 |

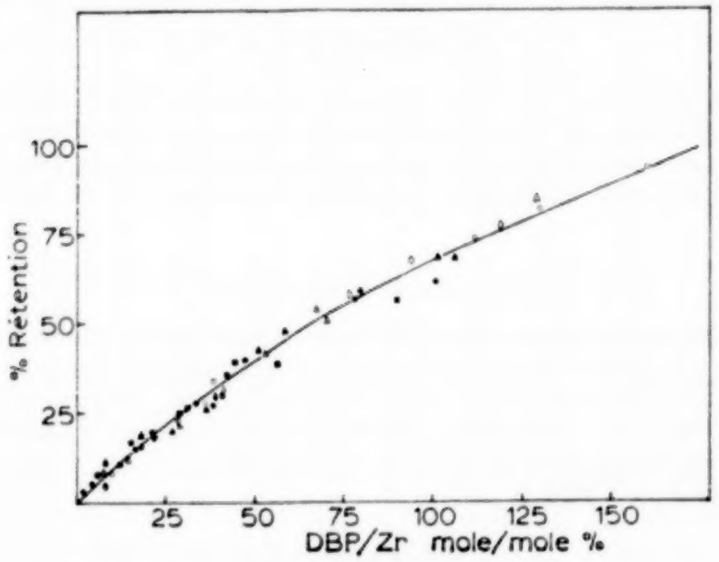

Fig. 5. Rétention en fonction du rapport DBP/Zr molaire.

| *Diluant* | *Zr* | *synthétique* | *vieillissement* |
|---|---|---|---|
| "white spirit" | 20 g/l | ○ | ● |
| "white spirit" | 3 g/l | △ | ▲ |
| xylène | 20 g/l | □ | ■ |
| hexane | 20 g/l | ◇ | ◆ |

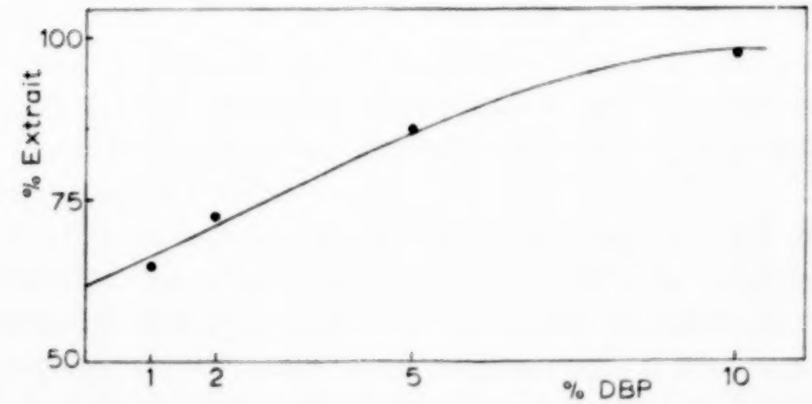

Fig. 6. Influence du dibutylphosphate sur l'extraction du zirconium. Solution aqueuse de zirconium à 20 g/l.

En conclusion, nous pouvons dire qu'il importe de débarrasser le solvant du zirconium qu'il contient, le plus rapidement et le plus complètement possible. À cet égard, une récupération à l'eau, en continu, est préférable à une récupération discontinue. L'expérience a montré que cette forme de récupération n'était cependant pas suffisante, et que périodiquement un lavage du solvant par l'acide sulfurique, puis par du carbonate, était nécessaire pour éliminer avec le zirconium, le dibutylphosphate formé.

## RÉSUMÉ

La seconde partie de cet article est consacrée plus spécialement au solvant. Les auteurs examinent tout d'abord les conditions de démixtion du mélange de tributylphosphate, de diluant et de zirconium, puis l'intéraction du zirconium et du tributylphosphate lorsqu'ils sont abandonnés en présence l'un de l'autre; on montre que le résultat essentiel de cette intéraction est la formation du phosphate dibutylique qui possède un fort pouvoir complexant à l'égard du zirconium.

## SUMMARY

The chemical equilibria governing the separation of zirconium from hafnium are considered with particular reference to the solvent. The conditions of separation of a mixture of tributylphosphate, diluent and zirconium have been studied as well as the interaction of tributylphosphate and zirconium. The latter results in the formation of dibutylphosphate which has a strong complexing capacity for zirconium.

## ZUSAMMENFASSUNG

Es werden die chemischen Gleichgewichte untersucht, von denen die Trennung des Zirkoniums vom Hafnium abhängig ist unter besonderer Berücksichtigung des Einflusses des Lösungsmittels. Die Bedingungen für die Phasenbildung eines Gemisches von Tributylphosphat, Verdünnungsmittel und Zirkonium wurden festgestellt. Es konnte ferner eine Reaktion zwischen Tributylphosphat und Zirkonium nachgewiesen werden, die zur Bildung von Dibutylphosphat führt, das mit Zirkonium einen Komplex bildet.

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# ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co*

## II. SOLVENT EXTRACTION

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(Received September 28th, 1960)

### INTRODUCTION (CHOICE OF THE SYSTEM)

An extensive literature on the concentration and separation of metals by solvent extraction is available. Reviews have been given by MORRISON AND FREISER[1], BABKO AND ZHAROVSKII[2] and WEST AND MUKHERJI[3]. Extractions with organic nitrogen and phosphorus compounds have been reviewed by WHITE[4]. The (discontinuous) extraction technique has the advantage of simplicity and speed.

Concentration is easily accomplished, especially when solvents with a low boiling-point are used.

Separation from macro-constituents is readily achieved. Mutual separations can be obtained in two ways: *(1)* by the application of several successive extracting agents and/or solvents (WEST[3]) or *(2)* with one agent and one solvent only, but using masking-agents and/or different pH values. Of course in both cases, mutual interferences of the extracting or masking agents must be avoided. Thus it is evident that a universal reagent, made selective by changes in the pH, is to be preferred.

Precipitation, under the circumstances required by the extraction process, should be prevented. This is especially important with biological ashes and in general with all samples containing a large excess of inorganic macro-constituents. It forms the main objection against the extraction of the halide and thiocyanate complexes, as these procedures usually require a concentrated solution of the respective anion in which precipitations readily occur.

Combination of extractions with quantitative techniques such as flame photometry, spectrophotometry, neutron activation etc., offers no problem. Combination with spectrophotometry is simple when the extracted complex has a characteristic light absorption, while combination with radiometric techniques is feasible, for example, when a radioactive reagent can be used for the extraction, or when the extracted metal complex can be exchanged with a radioactive metal.

In general however, combination with radiometric techniques (and also with polarography, titrimetry, etc.) poses several problems. Either the reagent used for the extraction should not be extracted or it should easily be evaporated or ashed.

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* Publication No. 128$^b$ of the Research Institute for Animal Husbandry ,,Schoonoord" Hoogt 10$^{bis}$, Utrecht (The Netherlands).

(The metal complex itself should also easily be ashed). These requirements are a serious objection against the use of aliphatic amines, organic phosphorous compounds, 8-hydroxyquinoline and thenoyltrifluoroacetone.

Only the reagents acetylacetone and diethyldithiocarbamate were considered to fulfill all the requirements mentioned above. Trifluoroacetylacetone could have been used but was not readily available. Xanthate could be used instead of the dithiocarbamate, but it does not allow the extraction of manganese.

Acetylacetone is universal and allows separations to be made by means of pH adjustment. The reagent is coextracted (and in fact is often used itself as a solvent for the metal complexes), but it can easily be evaporated. Metal acetylacetonates can be ashed. The use of acetylacetone as a radioactive reagent is uneconomical as a large excess is required for the extraction*. Radio-exchange of metal acetylacetonates has been studied but without success so far[5].

Diethyldithiocarbamate is also universal and allows separations to be made by means of pH adjustment. Only a small amount of the reagent is extracted. The metal complexes can easily be ashed. As a rather small excess of reagent is required, the application of the labelled diethyldithiocarbamate is feasible (and in fact has been used for the determination of cobalt[6]). The exchange of the lead from the lead diethyldithiocarbamate with labelled thallium(III) and the exchange of lead with $^{204}$Tl-diethyldithiocarbamate have both been applied for the determination of submicrogram amounts of lead[5,6].

## ACETYLACETONE

FREISER and his coworkers[7-14] have been very active in this field. WEST[3] used the reagent in combination with other extracting agents (including diethyldithiocarbamate) to achieve a systematical separation of a large group of metals. In general, discontinuous techniques were applied but extractions were never complete in one procedure, even when pure acetylacetone was used. Only molybdate and cobalt(III) were found[9,12] to be extracted below pH 0.0; iron(III) and copper were extracted at pH 2.0, but for zinc, lead and manganese higher pH values were required; cobalt(II) and iron(II) were not extracted at all.

## *Experimental*

### *Materials* (see also part I)

*Acetylacetone* (Merck *p.a.*) was neutralised daily by shaking with one volume of 0.01 *N* sodium hydroxide. All chemicals were again of reagent grade.

### *Apparatus*

Most extractions were carried out with the mixture 1:1 chloroform–acetylacetone in the pyrex glass shaking tubes shown in Fig. 1. Eight tubes were attached with chromium-plated clips to the platform of a home-made aluminium shaker (Fig. 2), the velocity of which could be regulated between 5 and 20 periods per minute. The tubes were filled in position I (the upper meniscus should stand between C and $C^1$) and emptied in position II. All operations with radio-active solutions were carried out in a shallow trough made of polyethylene.

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* Paper chromatographic separation of $^{14}$C-labelled metal acetylacetonates, which require only a small excess of the reagent, has been studied[5] without success: traces of the labelled reagent adhered to the paper and gave rise to a variable background.

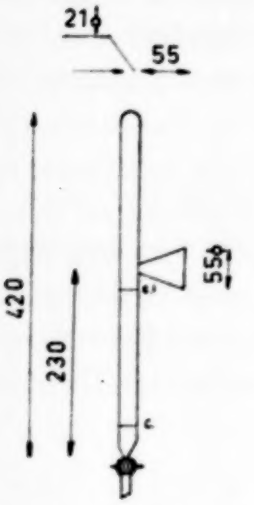

Fig. 1. Pyrex-glass shaking tube for discontinuous extractions.

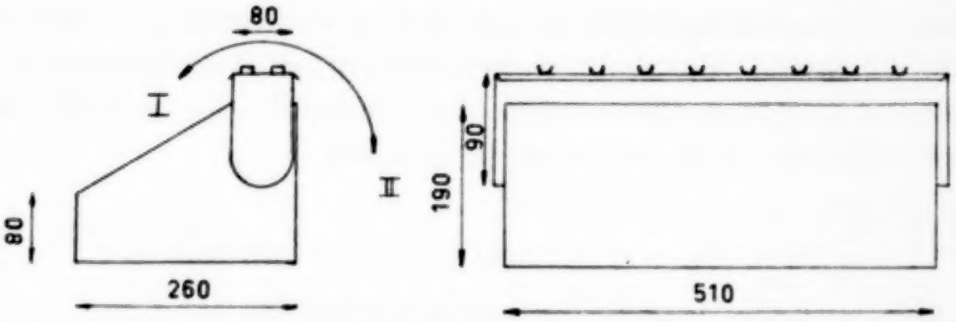

Fig. 2. Aluminium shaker for 8 tubes of Fig. 1.

*Pretreatment of the sample*

The ashing procedure was described in part I. Residues of perchloric acid had to be removed carefully here, as they interfered with the extraction (see STEINBACH[12]).

*Analytical methods*

The same methods were applied as in part I. For iron(III), flame photometry[15,16] or spectrophotometry of the extract can replace the tracer method. The methods of MARONI AND DUBOIS[17] and of CARTLEDGE[18], for the spectrophotometric determination of copper and manganese acetylacetonates respectively, were found to be unsatisfactory. Thus copper was determined as described in part I (after the evaporation and ashing of the extract).

## *Results*

Molybdenum was extracted from 6 *N* sulfuric acid (pH 0.8). As 0.5 ml of concentrated sulfuric acid was used for the ashing, the product had only to be diluted with 2.5 ml of water. With this small aqueous volume a small pill capsule made of PVC with a tightly fitting lid, and of diameter 25 mm and height 76 mm, was more convenient for the extraction. Pure acetylacetone was used instead of a mixture with chloroform, as it was more easily removed from the pill-case. With our procedure (see p. 134) two shakings sufficed for 98% extraction; less than 0.5% of the other trace elements was removed.

A similar result could be obtained for iron and copper at pH 2.0*. As the volume was increased by the neutralisation, either the pill-case (and pure acetylacetone) or the tubes shown in Fig. 1 (and acetylacetone-chloroform) could be used.

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* All pH values given are starting values. The final pH values were either higher (below pH 5) or lower (above pH 5) than these starting values.

A pH value between 7.5 and 9.5 was required to obtain similar results for manganese and lead. These metals were not extracted below pH 4.0* and 6.0 respectively.

The extraction of zinc and cobalt was incomplete under all circumstances. Only 40% of the zinc was extracted (between pH 6.0 and 9.5) from a solution of the ash of 1 g of dry cow liver. The extraction from a pure zinc chloride solution was only slightly better. For the cobalt, oxidation to cobalt(III) proved to be necessary and was best carried out with hydrogen peroxide at a pH between 8 and 9; the extraction itself was most effective between pH 4 and 5. In contrast to pure cobalt solutions, the cobalt from sample solutions was extracted only very incompletely (about 50%).

Cobalt(III) was unstable below pH 3 and thus extraction below this pH was negligible; but once it had formed, the cobalt acetylacetonate was stable even to acids**.

In conclusion, the acetylacetone extraction of molybdenum, iron, copper, manganese and lead from the solution of a biological ash is feasible, but cobalt and zinc are extracted only to an extent of 50% or less.

## DIETHYLDITHIOCARBAMATE

Studies with this reagent have been carried out by many authors and reviews have been published[19-23]. Dialkyl, pyrrolidine and other derivatives have also been applied. In general these compounds do not have many advantages, but some are more stable to acids than diethyldithiocarbamate.

### *Experimental*

(see also part I and Experimental p. 130)

All chemicals used were of reagent grade. Mercury solution: 0.1 *M* potassium sodium tartrate containing 160 μg of mercury(II) (as the nitrate) per ml, adjusted to pH 8.5 with sodium hydroxide. The ashing-procedure was as described in part I. Again radio-isotopes were applied to facilitate the evaluation of the results. Copper was determined spectrophotometrically with the reagent itself, following the method of CLULEY[23].

### *Results*

Experiments were again carried out with the ash of 1 g of dry cow liver. The tubes shown in Fig. 1, aqueous and organic volumes of 20 and 10 ml respectively, and a 10-fold excess of diethyldithiocarbamate over the total of the heavy metals were used. To prevent precipitations, 0.2 *M* potassium sodium tartrate was present. With 2 shakings of 5 min each, copper, lead and cobalt were completely extracted at pH values up to 14, zinc only up to 13, and iron and manganese up to 9. Molybdenum was extracted only below pH 5. Separation of copper, lead and cobalt could be obtained by back-extractions with potassium cyanide (Cu), and mercury(II) followed by potassium cyanide (Pb)***.

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* This is in contrast to STEINBACH[12], but in accordance with FREISER *et al.*[9]

** This extraordinary behaviour of cobalt was not clearly indicated by either STEINBACH[12] or FREISER *et al.*[9]

*** This technique was used by PŘIBIL *et al.*[25] for the spectrophotometric determination of microgram amounts of cobalt and by the present author[6] for the radiometric determination of submicrogram amounts of cobalt.

Separation of iron and manganese could not be obtained in a similar way however, although several masking agents were applied (including fluoride, pyrophosphate, citrate, sulfite, hydroxylamine, cysteïne, cysteïnamine and "Tiron"). As manganese would have to be determined in the presence of a large excess of iron (with most biological and many other samples), extractions with diethyldithiocarbamate alone were not satisfactory*.

## COMBINATION OF ACETYLACETONE AND DIETHYLDITHIOCARBAMATE

Successive extractions with acetylacetone (at pH 2.0) and diethyldithiocarbamate led to a satisfactory procedure. Fortunately the extractions with the diethyldithiocarbamate were only slightly influenced by the presence of the acetylacetone. In Fig. 3 the latter results are shown.

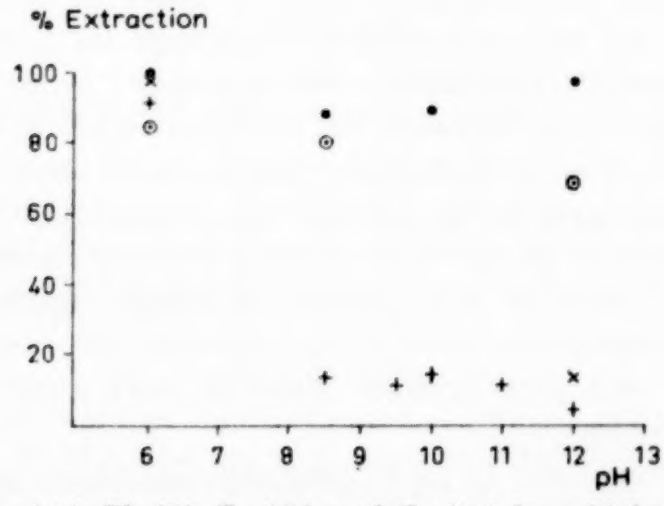

Fig. 3. Extraction of Mn (+), Pb (⊙), Zn (●) and Co (×) from biological ashes, with diethyldithiocarbamate and $CHCl_3$ (after the extraction of Fe and Cu with acetylacetone). Ammonium ion interferes with the extraction of Zn.

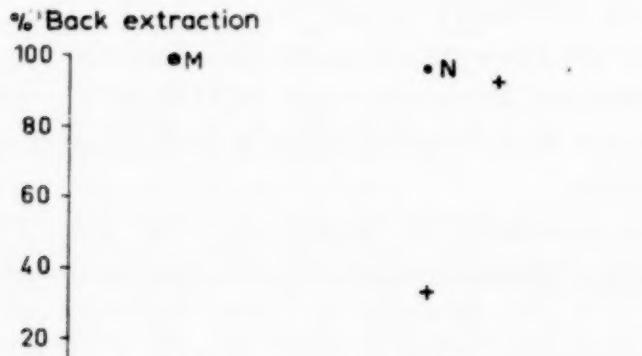

Fig. 4. Back-extraction of Mn (+), Pb (⊙), Zn (●) and Co (×) from the solutions of their diethyldithiocarbamate complexes in $CHCl_3$ with alkaline tartrate. M: Mercuric solution. N: Ammonia instead of sodium hydroxide. D: in darkness.

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* Iron could be retained in the aqueous sample solution by adding sodium fluoride up to 0.1 *N* after the extraction of the zinc. In this way Mn could be separated from Fe. The determination of Fe in the aqueous fluoride solution was complicated appreciably however.

Unfortunately a separation into the groups lead–zinc and cobalt–manganese (by extraction at pH 12 for instance) is not possible: the amounts of the latter metals lost in the lead–zinc fraction are too high. (The behaviour of cobalt is not in accordance with the literature. This may be due to the combined influences of the acetylacetone and the constituents of our sample solutions.)

Thus extraction of all four elements at pH 6.0 was chosen and back-extractions at different pH values were carried out to achieve separation. These back-extractions are shown in Fig. 4.

Obviously the best separation is achieved by successive strippings at pH 13 (Mn), pH 14 (Zn) and pH 8.5 with the addition of mercury(II) (Pb). The mercury diethyldithiocarbamate can be removed with potassium cyanide while the cobalt complex remains in the chloroform.

## PROCEDURE

Wet-ash and dilute with water to about 3 ml. Transfer to the pill-case and shake* during 2 min with 3 ml of acetylacetone. Centrifuge for 1 min at 1000 rev./min (ø 25 cm) to promote separation and remove the upper layer with a pipet. Repeat this extraction once (the "film" between the two layers is left in the aqueous fraction). Evaporate the acetylacetone and treat the residue with some bromine water (Mo).

Transfer the aqueous layer to the tube of Fig. 1, adjust with ammonia to pH 2.0 (thymol blue) and dilute to 20 ml. Add 10 ml of 1:1 acetylacetone–chloroform and shake for 5 min, with a velocity of 10 periods per minute, in the apparatus of Fig. 2. Remove the extract, repeat the extraction, evaporate the combined organic layers and treat the residue with some bromine water or with a mixture 1:1 nitric acid–hydrogen peroxide (Fe, Cu).

Neutralise the aqueous layer to pH 6 (bromothymol blue), add potassium sodium tartrate to give a 0.1 *M* solution and diethyldithiocarbamate in a tenfold excess over the remaining trace elements.

Shake for 5 min with 5 ml of chloroform, remove the extract and repeat the extraction.

Transfer the combined extracts to a pill-case and strip the chloroform by shaking for 2 min with 5 ml of the following successive solutions: (*1*) pH 13, (*2*) pH 14, (*3*) pH 8.5**, (*4*) pH 8.5, mercury(II) (see p. 132) and (*5*) pH 8.5, 1% potassium cyanide, all solutions containing 0.1 *M* potassium sodium tartrate and adjusted to the desired pH with sodium hydroxide.

These solutions then contain: *(1)* manganese, *(2)* zinc, *(3)* no trace elements, *(4)* lead and *(5)* mercury. Cobalt remains in the chloroform phase.

## CONCLUSIONS

The system chosen, a combination of acetylacetone and diethyldithiocarbamate, has some similarity with the extraction scheme of WEST[3]. For reasons which were discussed in the introduction, the extractions from acidic chloride and thiocyanate solutions, applied by WEST, had to be omitted. Furthermore our extractions with acetylacetone and diethyldithiocarbamate were carried out at higher pH values and several strippings were used by us to separate the diethyldithiocarbamate complexes. By the above method, all metals, except iron and copper are separated. Concentration of the trace elements and separation from the macro-constituents is accomplished. The organic complexes which are introduced can easily be removed.

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* For instance in a "Microid Flask Shaker"

** Solution *(3)* is required to ascertain the right pH for solution *(4)*; shaking with this solution for only a few seconds is sufficient.

## ACKNOWLEDGEMENTS

The author's thanks are due to Mrs. G. A. OVEZALL-KLAASEN and Miss J. H. F. F. BROEKMAN for valuable technical assistance.

## SUMMARY

Extractions with acetylacetone and diethyldithiocarbamate are described. Through the successive application of these reagents the constituents of biological ashes are concentrated and separated into the groups: *(1)* $MoO_4^{-2}$, *(2)* $Fe^{+3}$, $Cu^{+2}$, *(3)* $Mn^{+2}$, *(4)* $Zn^{+2}$, *(5)* $Pb^{+2}$, *(6)* $Co^{+3}$ and *(7)* $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, $SO_4^{-2}$, $PO_4^{-3}$.

## RÉSUMÉ

Des extractions au moyen d'acétylacétone et diéthyldithiocarbamate sont décrites, en vue d'une séparation des divers constituants des cendres biologiques (Fe, Cu, Zn, Pb, Mo, Co).

## ZUSAMMENFASSUNG

Es werden Extraktionen mit Acetylaceton und Diaethyldithiokarbamat beschrieben. Durch geeignete Anwendung dieser Reagenzien können die Bestandteile von biologischen Aschen in folgende Gruppen getrennt werden: *(1)* $MoO_4^{-2}$, *(2)* $Fe^{+3}$, $Cu^{+2}$, *(3)* $Mn^{+2}$, *(4)* $Zn^{+2}$, *(5)* $Pb^{+2}$, *(6)* $Co^{+3}$ und *(7)* $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, $SO_4^{-2}$, $PO_4^{-3}$.

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# INDIRECT OXIDIMETRIC DETERMINATION OF CERTAIN α-AMINO ACIDS WITH VANADIUM(V)

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(Received November 21st, 1960)

α-Amino acids which are smoothly oxidised quantitatively by certain 1,2-glycol splitting reagents such as periodic acid[1] and lead tetraacetate[2] are resistant to certain other oxidants such as cerium(IV)[3] and vanadium(V). The de-aminated products of the amino acids with nitrous acid, *i.e.* the α-hydroxy acids, can however be oxidised easily by these oxidants. TAKAHASHI *et al.*[3] have developed an indirect method for the determination of α-amino acids via oxidation of the de-amination products but the results are not strictly stoichiometric and empirical factors calculated from pure compounds are required. Studies on the oxidation of organic compounds by vanadate solution in these laboratories have shown that vanadate is a milder and more specific oxidant for organic compounds than cerium(IV). The present communication describes a study of the oxidation of the de-amination products of the α-amino acids with a view to developing a method for their determination; the reactions are more stoichiometric than with cerium(IV).

It has also been shown that pure vanadium pentoxide can be used as a primary standard.

## EXPERIMENTAL

### *Preparation and standardisation of vanadate solution from vanadium pentoxide*

Earlier workers[4,5] have recommended either ammonium vanadate or sodium metavanadate for the preparation of vanadate solutions. BISHOP AND CRAWFORD[5] have shown that pure ammonium vanadate can be used as a primary standard but it is generally preferred to standardise the solution before use. RAO *et al.*[4] converted ammonium vanadate to the sodium salt by boiling with slight excess of sodium carbonate till the smell of ammonia ceased and decomposed excess carbonate with acid but this method is laborious. Therefore it was thought better to use vanadium pentoxide for preparing sodium vanadate solution.

The vanadium pentoxide used in the present investigation was an A.R. sample supplied by Baker which was stated to have 100% assay. Analytically pure vanadium pentoxide can also be prepared by decomposing twice crystallized ammonium metavanadate in a platinum crucible in presence of air at a temperature of 400°–500° and storing the material in a desiccator. Vanadium pentoxide which consists of cinnabar red rhombic crystals, is only slightly soluble in water giving an acidic reaction, but dissolves freely in alkaline solution to form colourless vanadate solution. On acidification the solution turns yellow but does not reprecipitate at low concentrations (*cf.* $As_2O_3$). Solutions of exact strength can be prepared by this method and are free from ammonium ions. According to JANDER AND JAHR[6], polyvanadates exist as an equilibrium mixture in the solution depending on its pH. But this does not affect the usual oxidising properties of the vanadate solution.

The vanadate solution was prepared by shaking a weighed quantity of vanadium pentoxide in approximately 1.0 *N* sodium hydroxide until dissolution was complete. The solution was then diluted to the mark in a volumetric flask. The strengths of the solutions were checked by titrating against a standard ferrous ammonium sulphate solution, the strength of which was determined by potassium dichromate solution, N-phenylanthranilic acid being used as internal indicator. The results of the standardisation given in Table I indicate that the vanadium pentoxide can be used satisfactorily as a primary standard.

TABLE I

| *Vanadium pentoxide taken (g)* | *Vanadium pentoxide found (g)* |
|---|---|
| 9.0856 | 9.0910 |
| 8.8792 | 8.8600 |
| 10.1224 | 10.1340 |

### *Amino acid solutions*

Fresh 0.02 *M* solutions of pure amino acids (DL-alanine, DL-norleucine, and D-glutamic acid) were prepared by dissolving the requisite amount of pure amino acids in distilled water.

### *General procedure for de-amination and oxidation of amino acids*

To an aliquot of the amino acid solution in a 250-ml conical flask fitted with a reflux condenser, approximately 1 ml of 30% sodium nitrite solution and 10 ml of 3 *N* sulphuric acid together with 20 ml of distilled water were added and the solution was boiled till a drop of the solution gave no colour with starch-iodide paper. A known excess of 0.1 *N* vanadate solution was added and the overall acid concentration was adjusted to approximately 12 *N*. The solution was refluxed on a water bath for 30 min and then cooled. The excess of vanadate in the solution was determined by back-titration with standard ferrous ammonium sulphate solution potentiometrically or with *N*-phenylanthranilic acid as indicator. From the amount of vanadate consumed the equivalents of oxygen consumed per mole of the amino acid was determined. The results are given in Table II.

TABLE II

| *Amino acid* | *Amount of 0.02 M amino acid (ml)* | *Amount of 0.1 N vanadate solution (ml)* | *Equivalents of oxygen consumed per mole of amino acid* | |
|---|---|---|---|---|
| | | | *found* | *calculated* |
| DL-Alanine | 5.0 | 5 | 2.15 | 2 |
| DL-Norleucine | 4.0 | 5 | 2.03 | 2 |
| D-Glutamic acid | 3.5 | 5 | 4.32 | 4 |

From Table II it is evident that the equivalents of oxygen consumed correspond to the oxidation to formic acid and higher fatty acids according to the general equations:

$$\mathrm{RCH\,(NH_2)\,COOH} \xrightarrow{\mathrm{HNO_2}} \mathrm{RCH\,(OH)\,COOH} + \mathrm{N_2} + \mathrm{H_2O}$$

$$\mathrm{RCH\,(OH)\,COOH} \xrightarrow{\mathrm{O}} \mathrm{RCOOH} + \mathrm{HCOOH}$$

and that the reactions are more or less stoichiometric.

## DISCUSSION

It has been shown that the oxidation of the de-amination products of the α-amino acids with vanadate provides a more satisfactory method for their determination than oxidation by cerium(IV) and the use of empirical corrections can be eliminated. The success of the method depends to a very great extent on complete elimination of nitrous acid, on preventing the loss of the decomposition products of α-hydroxy acids, and on preventing further oxidation of formic acid. That formic acid is not oxidised to a measurable extent under these conditions is well established and the loss of volatile decomposition products, *i.e.* the aldehydes and the formic acid, can be minimised by circulating cold water through the reflux condenser. The method can also be applied for the determination of a mixture of two or more amino acids.

## ACKNOWLEDGEMENT

The authors express their thanks to Prof. K. P. Haldar, Head of the Department of Chemistry, for his keen interest in the work.

## SUMMARY

A method for preparing standard vanadate solution using pure vanadium pentoxide as primary standard is described. The determination of certain α-amino acids by oxidation of their de-amination products with standard vanadate solution is studied.

## RÉSUMÉ

Une méthode est proposée pour le dosage de certains acides α-aminés; on traite la solution à analyser par une solution de vanadium(V), dont on titre l'excès par le fer(II).

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung gewisser α-Aminosäuren durch Behandlung mit einer Vanadium-(V)-lösung, deren Ueberschuss mit einer Eisen-(II)-lösung zurücktitriert wird.

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# QUANTITATIVE ASPECTS OF THE OXIDATION OF ALIPHATIC ALCOHOLS BY POTASSIUM PERMANGANATE

## I. METHANOL AND ETHANOL

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(Received October 26th, 1960)

Further investigation of the use of redox titrations for the determination of simple aliphatic alcohols was prompted by the unsatisfactory features of the available volumetric methods. Several workers[1-4] have reported the use of dichromate for the determination of methanol, ethanol and 2-propanol; the present paper deals with quantitative aspects of the oxidation of methanol and ethanol by acidified permanganate solutions. Earlier workers have examined the use of acidified and alkaline solutions of permanganate for such determinations[4], but none of these methods appears to be very satisfactory and the effect of catalysts does not seem to have been studied. In the present work, conditions for the quantitative conversion of methanol to carbon dioxide have been established for fairly low concentrations of this alcohol, but no simple stoichiometric relationship could be found for the oxidation of ethanol under similar conditions.

## EXPERIMENTAL

All reagents used were of analytical reagent grade. Solutions of sodium thiosulphate,

TABLE I

COMPOSITION OF REACTION MIXTURES INVESTIGATED

All molarities refer to reaction mixture

| *Molarity of alcohol* | | *Moles/mole of alcohol* | | *Molarity of catalyst* | | *Reaction temperature (°C)* | *Optimum reaction time (h)* |
|---|---|---|---|---|---|---|---|
| *MeOH* | *EtOH* | *$KMnO_4$* | *$H_2SO_4$* | *$Mn^{+2}$* | *Ammonium molybdate* | | |
| 0.003 | — | 0.60 | 100.0 | 0.0015 | — | 45 | 24 |
| 0.01 | — | 2.84 | 94.8 | 0.0200 | — | 45 | 12 |
| 0.01 | — | 2.84 | 96.7 | — | 0.0398 | 50 | 4 |
| 0.01 | — | 2.69 | 102.5 | — | 0.0398 | 60 | 1¾ |
| 0.01 | — | 5.82 | 92.0 | — | 0.0398 | 60 | 1 |
| 0.005 | — | 2.94 | 208.2 | — | 0.0796 | 60 | 2½ |
| 0.005 | — | 5.87 | 182.7 | — | 0.0796 | 60 | 2 |
| 0.0025 | — | 5.68 | 413.8 | — | 0.1582 | 60 | 3 |
| 0.0025 | — | 9.35 | 370.2 | — | 0.1582 | 60 | 2 |
| — | 0.01 | 2.70 | 91.4 | — | 0.0398 | 18 | 3 |

iodine, sulphuric acid and potassium permanganate were standardised against potassium iodate by conventional methods.

### *Oxidation procedure*

Solutions of the reactants and catalyst were mixed in a 250-ml flask, fitted with a ground-glass stopper, which was immersed in a thermostat at the required temperature. Typical reaction conditions with optimum reaction times are shown in Table I.

### *Determination of permanganate consumed*

After the reaction, excess of permanganate was determined iodometrically, the mixture being diluted with an equal volume of water and cooled rapidly to room temperature before addition of potassium iodide solution. Appreciable thermal decomposition of permanganate occurred during the reaction period, especially at the higher temperatures used; an appropriate correction was, however, determined in blank experiments and applied.

### *Determination of carbon dioxide*

In certain cases (Tables II and III) the carbon dioxide produced during the oxidation was measured directly. Carbon dioxide-free air was drawn slowly through the

TABLE II

EXTENT OF CONVERSION OF METHANOL TO CARBON DIOXIDE FROM PERMANGANATE CONSUMPTION AND FROM EVOLVED CARBON DIOXIDE

Temperature: 60°

| *Reaction mixture* | | *Uptake of $KMnO_4$ (moles/mole MeOH)* | | *% Methanol completely oxidised from* | |
|---|---|---|---|---|---|
| *Molarity of MeOH* | *Moles $KMnO_4$ per mole MeOH* | *Mean value (10 determinations)* | *Maximum deviations* | *$KMnO_4$ uptake* | *Direct determination of evolved $CO_2$* |
| 0.0025 | 9.35 | 1.23 | ± 0.02 | 102.5 | 102.8 |
| 0.005 | 5.87 | 1.21 | ± 0.01 | 100.8 | 99.6 |
| 0.010 | 2.69 | 1.12 | + 0.01<br>— 0.02 | 93.3 | 93.4 |

TABLE III

EXTENT OF CONVERSION OF ETHANOL TO ACETIC ACID AND CARBON DIOXIDE

Temperature: 18°

| *KMnO. uptake for* | | *Wt. of evolved $CO_2$ (mole/mole EtOH)* | *$KMnO_4$ uptake* | |
|---|---|---|---|---|
| *Complete reaction* | *Reactions other than stages a and b* | | *Needed to form evolved $CO_2$* | *Due to "induced decomposition"* |
| 0.965 | 0.165 | 0.029 | 0.023 | 0.142 |

* Initially in reaction mixture: $[EtOH] = 0.01\ M$; $[MnO_4^-] : [EtOH] = 2.70$. Moles EtOH present $= 5.02 \cdot 10^{-4}$

** All $KMnO_4$ uptake values are in moles $KMnO_4$/mole EtOH in reaction mixture. Reaction stages *a* and *b* refer to the oxidation sequence given for ethanol (see Discussion).

reaction mixture and then through a series of wash-bottles containing barium hydroxide solution. With 0.01 $M$ alcohol concentrations, barium carbonate was precipitated from a saturated barium hydroxide solution, filtered off, dried and weighed. With more dilute alcohol solutions, excess of 0.05 $N$ barium hydroxide solution was titrated with 0.05 $N$ hydrochloric acid, with phenolphthalein indicator; carbon dioxide-free nitrogen was passed over the hydroxide solution and the acid was added slowly, with vigorous shaking, to minimise reaction with the barium carbonate.

### *Determination of carbon monoxide*

Carbon dioxide-free air was bubbled through the reaction mixture, as above, and then passed through two U-tubes containing "Sofnolite", to absorb any carbon dioxide, and magnesium perchlorate. Hopcalite (activated manganese dioxide) at 120° was then used to convert carbon monoxide to carbon dioxide, which was absorbed in saturated barium hydroxide solution and determined gravimetrically as barium carbonate.

### *Detection of formaldehyde*

Samples of reaction mixtures containing methanol and acidified permanganate were withdrawn at intervals. The permanganate colour was discharged with sulphur dioxide, and SCHRYVER's test[5] for formaldehyde was applied. Blank tests showed that sulphur dioxide did not interfere with the test.

## RESULTS AND DISCUSSION

### *Choice of catalyst*

Exploratory work showed that a 0.01 $M$ solution of methanol is not appreciably oxidised by acidified permanganate after 24 h at room temperature, but that the reaction is catalysed by manganese(II). Oxidation is extensive with this catalyst at 45°, but variable results (reproducibility ± 3%) were obtained, possibly due to the competitive reaction between permanganate and manganese(II)[6], and an alternative catalyst was therefore sought. Molybdate and vanadate ions were tested and quanti-

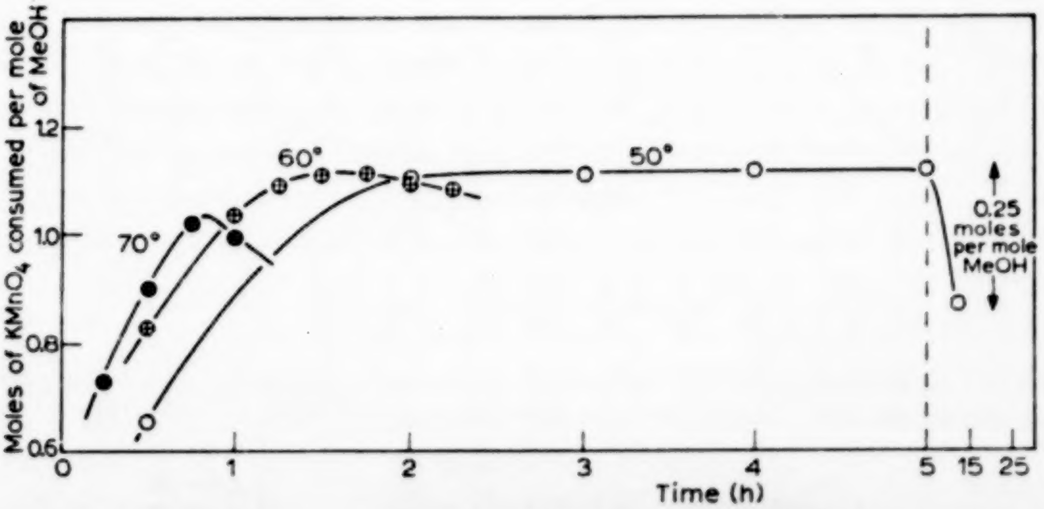

Fig. 1. The influence of temperature on rate of permanganate consumption by methanol. [MeOH] = 0.01 $M$; moles MeOH initially present = $5 \cdot 10^{-4}$; [$KMnO_4$] : ○ = 0.0284 $M$, ⊕ and ● = 0.0269 $M$.

tative investigations showed that ammonium molybdate was superior to manganese(II). Thus, oxidation of 0.01 *M* solutions of methanol at 60°, and of ethanol at room temperature, gave titration values which were reproducible to ± 0.5%.

*Choice of reaction temperature*

Variation with temperature of the time required for maximum uptake of permanganate by an 0.01 *M* solution of methanol is shown in Fig. 1. A temperature of 60° was chosen for the oxidation of less than 0.01 *M* methanol solutions because the maximum uptake of permanganate was then obtained after only 1–2 h.

In 0.01 *M* solution, ethanol was oxidised more rapidly than methanol and the optimum reaction time at room temperature was only 3 h (Table I). This result agrees with observations on the relative rates of 'induced oxidation' of aliphatic alcohols by acidified permanganate[7].

*Stoichiometry*

*(a) Methanol.* Total oxidation of methanol by permanganate probably proceeds by the series of reactions:

$$CH_3OH \xrightarrow{a} HCHO \xrightarrow{b} HCOOH \xrightarrow{c} CO_2 + H_2O$$

each stage involving one atom of oxygen. The existence of stage *a* was indicated by a positive test for formaldehyde, during the first 15 min of the oxidation of a 0.01 *M* solution of methanol.

The amounts of permanganate needed to oxidise methanol in various concentrations were determined by allowing the reaction to proceed at 60° in the presence of the catalyst, until the residual oxidising power remained constant. The excess of oxidising agent was varied for each of the methanol concentrations studied (see Fig. 2).

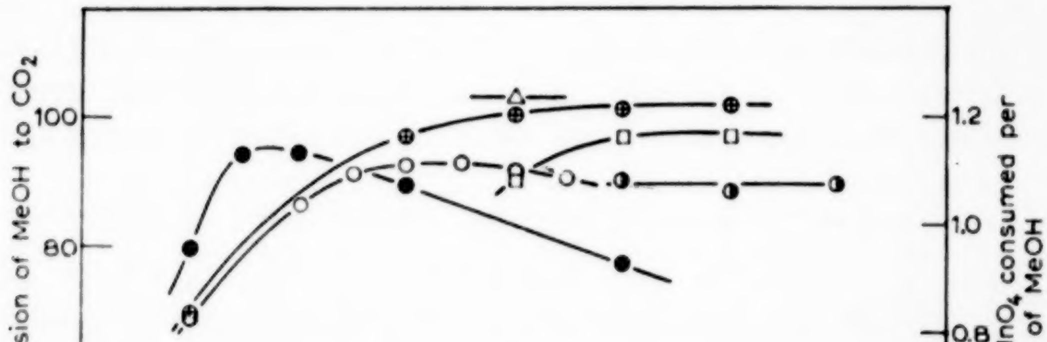

Fig. 2. Influence of concentrations of methanol and permanganate on extent of conversion of methanol to carbon dioxide. Temperature = 60°.

| [MeOH] | $[MnO_4^-]$ : [MeOH] |
|---|---|
| 0.01 *M* | 2.69 ○ |
| | 5.82 ● |
| 0.005 *M* | 2.94 ◑ |
| | 5.87 ⊕ |
| 0.0025 *M* | 5.68 □ |
| | 9.35 △ |

After reaching a maximum value, the consumption of permanganate decreased with time, apparently because of an increased rate of thermal decomposition of permanganate. The decomposition with time of 0.0284 *M* permanganate in blank experiments at 50° is shown in Fig. 3.

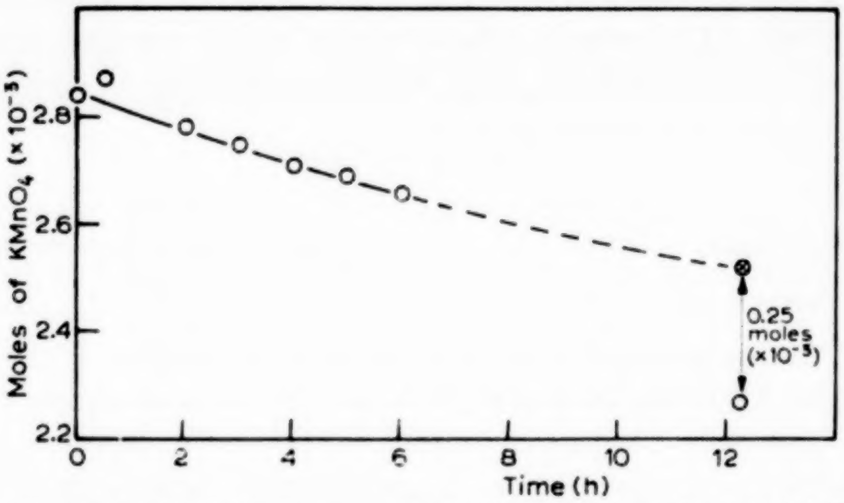

Fig. 3. Decrease in concentration of permanganate in "blank" experiments (*cf.* Fig. 1 and Table I). Temperature = 50°; $[MnO_4^-]$ = 0.0284 *M*; $[H_2SO_4]$ = 0.967 *M*; [Molybdate ion] = 0.0398 *M*.

The oxidising power of the 'blank' solution after about 12 h was 0.25 mole ($\times 10^{-3}$) of permanganate less than the extrapolated value, a decrease closely comparable with the decline in permanganate uptake observed in the reaction solution (Fig. 1). This decomposition of permanganate may well occur on the surface of precipitated manganese dioxide[8-10].

It can be seen from Fig. 2 that, when 0.005 *M* and 0.0025 *M* solutions of methanol were treated with a six- and nine-fold excess of permanganate respectively, the uptake of permanganate agreed well with the theoretical requirement (1.2 mole $KMnO_4$/mole MeOH). Direct determination of the evolved carbon dioxide confirmed that quantitative conversion of methanol to carbon dioxide had been achieved (Table II).

When a 0.01 *M* solution of methanol was treated with a three-fold excess of oxidant, the uptake of permanganate was 1.12 mole $KMnO_4$/mole MeOH, which corresponded to conversion of 93.3% of the alcohol to carbon dioxide and was confirmed by direct gravimetric determination of the carbon dioxide evolved (Table II). Gravimetric determination of carbon monoxide in the evolved gases showed that only traces were formed (equivalent to $< 0.5\%$ of the total carbon dioxide evolved). The extent of oxidation of methanol was only slightly increased by increasing the excess of oxidant; *e.g.* with a six-fold excess the uptake was only 1.13 mole $KMnO_4$/mole MeOH corresponding to 94.2% conversion to carbon dioxide.

The above experiments show that the extent of oxidation of methanol to carbon dioxide is increased by dilution of the methanol, and by the use of a larger excess of oxidant. In terms of the proposed reaction path, the results obtained suggest that, whilst stage *a* is fast and either stage *b* or *c* is rate determining, stage *b* competes with a process *d*: $n\mathrm{HCHO} \rightarrow (\mathrm{HCHO})_n$, which leads to the formation of an acid-stable polymer[11]. Thus:

$$\begin{matrix}\text{Total rate of} \\ \text{HCHO consumption}\end{matrix} = \begin{matrix}\text{Rate of oxidation} \\ \text{via stage } b\end{matrix} + \begin{matrix}\text{Rate of polymerisation} \\ \text{via stage } d\end{matrix}$$

$$= k_1 \cdot [\mathrm{HCHO}]^x \cdot [\mathrm{MnO_4^-}]^y + k_2 \cdot [\mathrm{HCHO}]^z$$

It can be seen that successful competition of process *b* with process *d* would be favoured by decreasing the concentration of methanol (and hence of formaldehyde formed via stage *(a)*) and increasing that of permanganate.

*(b) Ethanol.* The oxidation of a 0.01 $M$ solution of ethanol by a three-fold excess of permanganate, in the presence of ammonium molybdate catalyst, was investigated at room temperature. When the oxidising power of the residual solution reached a constant value, 0.965 mole $KMnO_4$/mole EtOH were found to have been consumed.

The probable course of the oxidation is:

$$CH_3.CH_2OH \xrightarrow{a} CH_3.CHO \xrightarrow{b} CH_3.COOH \xrightarrow{c} 2CO_2 + 2H_2O$$

in which each of the stages *a* and *b* require one atom of oxygen, whilst stage *c* requires 4 atoms of oxygen. Thus, the observed permanganate consumption suggests that, in addition to the complete oxidation of ethanol to acetic acid, requiring 0.8 mole $KMnO_4$/mole EtOH, partial oxidation of acetic acid to carbon dioxide had occurred, requiring a further 0.165 mole $KMnO_4$/mole EtOH (Table III). Gravimetric determination (as barium carbonate) of the carbon dioxide evolved showed that conversion of acetic acid to carbon dioxide accounted for only 0.023 mole $KMnO_4$/mole EtOH (Table III), thus leaving an unaccounted uptake of 0.142 mole. Since more extensive precipitation of manganese dioxide was observed in the reaction mixture than in blank experiments, the discrepancy may be due to an 'induced decompostion' of permanganate promoted by the ethanol.

## CONCLUSIONS

Manganese(II) and molybdate ions effectively catalyse the oxidation of simple alcohols by acidified potassium permanganate solution, the molybdate being superior in giving more reliable results. With molybdate catalyst and under the conditions described, the reaction may conveniently be used to determine methanol in solutions of fairly low concentration. The reproducibility for the concentrations studied is within $\pm$ 3%. For more concentrated methanol solutions and for ethanol solutions the reaction is non-stoichiometric, apparently due to competing side-reactions.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge his gratitude to Dr. C. F. Cullis of Imperial College for his unfailing interest and much valuable discussion, to W. G. Northcroft for assistance with experiments involving formaldehyde and to Shell International Petroleum Company Limited and The Royal Society for grants in respect of materials and apparatus.

## SUMMARY

The quantitative oxidation of methanol and ethanol by acidified potassium permanganate solution has been studied. Molybdate is superior to manganese(II) as the catalyst. In fairly dilute methanol solutions a large excess of permanganate oxidises the alcohol quantitatively to carbon dioxide. With ethanol, oxidation proceeds beyond the acetic acid stage but the further reaction is not stoichiometric.

## RÉSUMÉ

Une étude a été effectuée sur l'oxydation des alcools méthylique et éthylique par le permanganate de potassium en milieu acide. Comme catalyseur, le molybdate s'est montré supérieur au manganèse (II).

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die quantitative Oxydation von Methanol und Äthanol mit saurer Kaliumpermanganatlösung. Als Katalysator erwies sich Molybdat dem Mangan-(II) überlegen. Bei Aethanol verläuft die Oxydation nicht stöchiometrisch.

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*Anal. Chim. Acta*, 25 (1961) 139–145

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# 1,8-DIHYDROXYANTHRAQUINONE AS A REAGENT FOR BORIC ACID AND ITS USE IN THE ANALYSIS OF PHARMACEUTICAL GRADE GLASS

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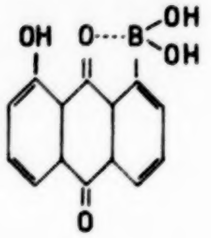
(Received September 28th, 1960)

The need to evaluate traces of boric acid, amounting to only a few $\mu$g, arising from hydrolytic transfer from pharmaceutical glasses, has led to a search for a highly sensitive procedure which would be simple to apply for quantitative work.

The best known methods in the literature are those which depend on the enhancement of the acidity of boric acid by polyhydroxy compounds, *viz.* glycerine[1,2], mannitol[3,4], pentamethylenequercitol[5], levulose, invert sugar or propylene glycol[6]. Such reactions may be made more sensitive by the use of potentiometric methods[7], high frequency methods[8,9], polarographic methods[10], polarimetric methods with tartaric acid[11] or complexometric methods[12]. The reaction between boric acid and fluoride in which hydroxyl ions are released, has been utilized colorimetrically[13]. The reaction between iodide and iodate with starch in presence of boric acid can only be used qualitatively[14]. In any case, all these methods require extractions, prior decompositions or titrations of very dilute solutions and so are unsuitable for rapid routine work.

1,8-Dihydroxyanthraquinone was investigated therefore as a reagent for boric acid.

It belongs to the hydroxyanthraquinone group and forms with boric acid in the presence of sulfuric acid a peri-hydroxy compound with heterovalent inner bonds[15]; the sulfuric acid acts as a dehydrating agent. The actual composition of the complex formed is:



Various anthraquinone derivatives have already been described for the detection of boric acid[16]. For example, purpurin (1,2,4-trihydroxyanthraquinone) shows an identification limit of 1 $\mu g$ of boron, alizarin S (1,2-dihydroxyanthraquinone sulfonic acid) shows a limit of 0.60 $\mu g$ of boron, and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) 0.06 $\mu g$ of boron. All these reagents are eminently suitable for the detection of boric acid in glass containers intended for pharmaceutical use, and quinalizarin is particularly sensitive, but none of the reagents mentioned yields a color intensity which is proportional to the boric acid concentration.

On the other hand, 1,8-dihydroxyanthraquinone, which is widely used as a cathartic under various trade names such as Istizin, Chrysazin, etc., and is readily available in a pure form, is almost as sensitive as quinalizarin and turns distinctly from brilliant red to purple red on addition of boric acid. Since the color formed is not pure, but rather a superposition of two colors, Beer's law is not obeyed at the maximum absorbancies at 340 and 580 m$\mu$, but satisfactory results can be obtained at the latter wavelength if a calibration curve is used. Moreover, 1,8-dihydroxyanthraquinone forms a bright pink fluorescent complex with boric acid which can be utilized quantitatively although the sensitivity is lower than the spectrophotometric reaction.

The method proposed is extremely simple and can be used in the cold; heating increases both the absorbance and the fluorescence slightly, but the relationship between the boric acid concentration and the measurement is then less regular. The color is reasonably stable and readings can be made between the 30th and 60th min, or within 2 h if a slight decrease in color intensity is allowed for.

The reaction has been examined for the detection and determination of boric acid from pharmaceutical grade glass ampoules, the qualitative tests being carried out on whole ampoules and the quantitative tests on powdered glass. When the sensitivity of the 1,8-dihydroxyanthraquinone reaction is compared with that of the abovementioned reagents of the anthraquinone group, it is possible to establish the limits of boric acid for a good grade glass.

## EXPERIMENTAL

### *Apparatus*

Spectrophotometer C.G.A. model 200/23. Fluorimeter C.G.A. C/S model 2/3.

### *Reagents*

1,8-Dihydroxyanthraquinone, 0.2% in concentrated sulfuric acid. 1,2,4-Trihydroxyanthraquinone, 0.5% in concentrated sulfuric acid. 1,2-Dihydroxyanthraquinone-3-sulfonic acid, 0.2% in concentrated sulfuric acid. 1,2,5,8-Tetrahydroxyanthraquinone, 0.01% in concentrated sulfuric acid.

### *Procedures*

*Spectrophotometric determination.* Solutions containing 0.1, 0.2, 0.3........ µg of boric acid per ml were prepared in concentrated sulfuric acid containing 0.2 % 1,8-dihydroxyanthraquinone reagent. The absorbancies were read at 580 mµ against the blank reagent between 30 min and 1 h after mixing. The calibration curve was prepared in this way (Fig. 1).

*Fluorimetric determination.* Solutions were prepared in the same way as for the spectrophotometric method but the amounts of boric acid taken were 0.5, 1.0, 1.5..... µg/ml. The readings were taken using a blue filter 20–40 min after mixing.

### *Application for the method to the detection and determination of boric acid in pharmaceutical grade glass*

*Qualitative test.* Dilute one drop of the several anthraquinone reagents under consideration with 0.5 ml of concentrated sulfuric acid for ampoules up to 3 ml and

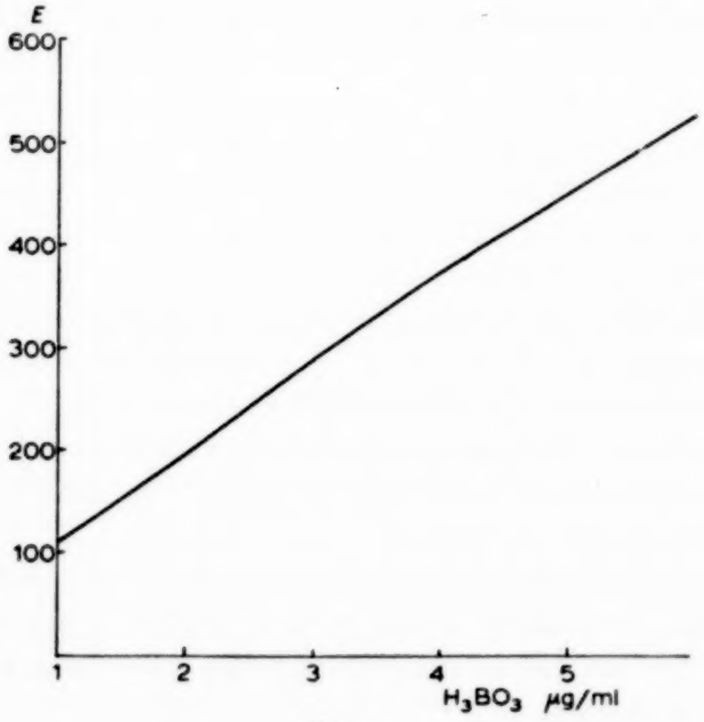


Fig. 1.

TABLE I

BEHAVIOUR OF A GOOD PHARMACEUTICAL GRADE GLASS WITH ANTHRAQUINONE REAGENTS

| *Reagent* | *Time for color change* | *Tone of color* |
|---|---|---|
| 1,2,4-Trihydroxyanthraquinone (Purpurin) | None within 24 h | From red to cherry red (not clean) |
| 1,2-Dihydroxyanthraquinone-3-sulphonic acid (Alizarins) | Slight within 30 min | From yellow to red (clean) |
| 1,8-Dihydroxyanthraquinone (Istizin, Crisizin) | Slight within 5 min | From red to purple red (clean) |
| 1,2,5,8-Tetrahydroxyanthraquinone (Quinalizarin) | 50% of the ampoules change color within 5 min | From purple to light or sky blue (clean) |

with 1 ml of concentrated sulfuric acid for larger ampoules or containers. Heat gently over a moving flame. The color changes obtained are described in Table I.

Thus, if the times for the various color changes are compared, a limit for the boric acid surface losses or transfers for a pharmaceutical grade glass can be established. Quinalizarin and Istizin are sufficient for this purpose; in addition to reducing the observation times, this allows the detection of boric acid and the determination of a maximum limit.

It is possible to state therefore that an acceptable pharmaceutical grade glass must satisfy the last two tests shown in Table I.

*Determination of boric acid in a pharmaceutical grade glass.* Crush the glass in a bronze mortar and remove any metallic particles by passing a magnet several times over it. Collect the glass powder which passes through a No. 35 sieve but is retained on a No. 55 sieve. Wash by decantation with 15-, 10- and 10-ml portions of water and with two 10-ml portions of ethanol, draining well each time. Dry at 120° for 30 min.

The glass particles thus obtained allow easy decantation: a smaller size, *i.e.* 80/100, yields sulfuric acid extracts which must be cleared by centrifugation and which increase the extraction by a mere 10–15%.

Weigh 15 g of the glass powder so prepared and transfer it to a 50-ml frosted heat-resistant glass flask, add concentrated sulfuric acid to 4/5 of the volume and leave for 12 h at room temp., shaking gently at frequent intervals. Fill at the same time a glass flask (without powdered glass) with concentrated sulfuric acid nearly to the mark, keeping it for use as blank.

After 12 h, add 1 ml of 1,8-dihydroxyanthraquinone reagent and bring to the required volume with concentrated sulfuric acid. Treat the flasks containing the powdered glass under test, the standard and the blank in the same way. Take readings against the reagent blank at 580 m$\mu$, as mentioned elsewhere. Use old glassware, whose boric acid surface transfers are absolutely negligible and do not therefore interfere with an accurate determination. For the calculation bear in mind that the 15 g of powdered glass is usually equivalent to 7.5 ml; the sulfuric acid extract inside a 50-ml glass flask corresponds to 42.5 ml.

Iron(III), nickel(II), cobalt(II) and chromium(III) do not interfere up to a quantity corresponding to half of the boric acid, and only slightly when they reach an equal amount. Therefore, an evaluation of boric acid contents in colored pharmaceutical grade glass is possible.

We have tested about 30 pharmaceutical grade glasses of different production, both

TABLE II

| *Weighed No. 35–55 glass powder* | *Sample No.* | *$H_3BO_3$ transfer $\mu g$* |
|---|---|---|
| g 15 | 1 | 61 |
| g 15 | 2 | 66 |
| g 15 | 3 | 56 |
| g 15 | 4 | 157 |
| g 15 | 5 | 103 |
| g 15 | 6 | 122 |
| g 15 | 7 | 38 |
| g 15 | 8 | 29 |

recent and old, and we have ascertained that a good pharmaceutical grade glass, in the standard conditions of the above-described determination, has a maximum transfer of 60–70 μg of boric acid for 15 g of No. 35–55 powdered glass, obtained from ordinary ampoules. Finished and stamped pharmaceutical grade glass, used for antibiotic containers, yield even lower boric acid transfer values.

Typical data are summarized in Table II.

In conclusion, 1,8-dihydroxyanthraquinone permits the evaluation of boric acid in glasses and the determination of limit characteristics for a good grade product suitable for pharmaceutical use, as established by the following tests.

*Qualitative test.* A change in color of quinalizarin reagent, under the standard conditions, of over 50% of the ampoules or containers within 5 min can be tolerated. The Istizin reagent should not change color before 5 min.

*Quantitative test.* 15 g of glass powder under the standard conditions, should yield not more than 60–70 μg of boric acid, when Istizin is used as the reagent.

## SUMMARY

1,8-Dihydroxyanthraquinone is proposed as an organic reagent for boric acid. The color change obtained is more useful for the determination of boric acid than those with other reagents of the anthraquinone group. The method is applied to the determination of boric acid transfers from pharmaceutical grade glass.

## RÉSUMÉ

La dihydroxy-1,8-anthraquinone est proposée comme réactif pour l'identification et le dosage de l'acide borique, en particulier dans le verre destiné à des usages pharmaceutiques.

## ZUSAMMENFASSUNG

Zum Nachweis und zur Bestimmung von Borsäure, besonders in Glasbehälter für pharmazeutische Zwecke, wird die Reaktion der Borsäure mit 1,8-Dihydroxy-anthrachinon vorgeschlagen.

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*Anal. Chim. Acta*, 25 (1961) 145–149

# APPLICATIONS DE LA CHÉLATOMÉTRIE

## VI. DOSAGE VOLUMÉTRIQUE DES *vic*-DIOXIMES

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avec la collaboration de F. VIEILLET pour la partie expérimentale

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(Reçu le 10 décembre, 1960)

### HISTORIQUE ET PRINCIPE

On connaît l'intérêt que les *vic*-dioximes présentent en chimie analytique minérale pour la détection et le dosage de plusieurs métaux. TSCHUGAEFF, le premier, puis BRUNK et, après eux, de nombreux autres ont décrit des méthodes gravimétriques, colorimétriques ou volumétriques de dosage du nickel, du palladium, du bismuth, du cobalt et du fer utilisant la diméthyl-glyoxime, la méthyl-éthyl-glyoxime, la méthyl-benzyl-glyoxime, les diphényl-glyoximes ou "benzyl-dioximes", la difurile-glyoxime et les cyclohexane, cycloheptane et cyclodecane-1,2 dioximes.

Les *vic*-dioximes présentent en outre des propriétés chimiques intéressantes en synthèse, ouvrant la voie notamment aux furoxannes ou oxadiazoles[1-8].

Peu de procédés ont été décrits pour l'estimation quantitative de ces réactifs; les seuls dont nous ayons connaissance reposent, soit sur une deshydrogénation au moyen de l'iode en présence d'un sel mercurique[1] — et cette dernière méthode présente le désavantage d'être perturbée en présence des monoximes des dicétones, et, d'une façon générale, en présence des oximes, lesquelles ont justement toutes les chances d'être rencontrées comme impuretés dans les dioximes — soit sur une gravimétrie au moyen d'un sel de nickel[9,10]; le seul procédé volumétrique utilisant un sel de nickel consiste à redissoudre le dioximate dans un acide pour permettre le dosage de l'hydroxylamine après hydrolyse [11,12] ce qui nécessite le transfert du précipité avec les inconvénients que comporte cette opération.

Nous avons préféré précipiter le dioximate par une quantité connue et en excès d'une solution d'acétate de nickel et après filtration, mesurer cet excès dans le filtrat en utilisant l'éthylène-diamino-tétracétate disodique ou "Chélate disodique" et la murexide qui nous avaient déjà donné satisfaction dans des travaux précédents[13a,c].

### RÉACTIFS

*Murexide à 1%*

On pèse 0.1 g de murexide, ajoute 10 g de chlorure d'ammonium bien sec et broie le tout intimement au mortier.

*Chélate disodique M/50*

On pèse 7.4 g d'éthylène-diamino-tétracétate disodique qu'on dissout dans un peu d'eau distillée fraîchement bouillie et complète à un litre exactement avec cette même eau. On détermine la molarité de cette solution à partir d'un poids connu de magnésium ou de zinc métalliques chimiquement purs en utilisant le noir Eriochrome T comme indicateur ou à partir d'une solution décinormale de nitrate d'argent en présence de tétracyano-nickelate de potassium et de murexide[14].

*Acétate de nickel M/5*

Dans 180 ml d'eau distillée on dissout 12.5 g de $Ni(CH_3COO)_2 \cdot 4H_2O$; on complète à 250 ml au moyen d'eau distillée. La molarité de la solution est mesurée de la façon suivante: On prélève au moyen d'une pipette 25 ml qu'on laisse couler dans une fiole jaugée de 250 ml et ajoute 50 ml d'ammoniaque; on complète jusqu'au trait de jauge avec de l'eau distillée; on agite pour homogénéiser la solution et prélève 25 ml (au moyen d'une pipette) qu'on laisse couler dans une fiole d'Erlenmeyer ou un bécher et auxquels on ajoute environ 0.3 g de murexide à 1%; on coule la solution de chélate préparée comme ci-dessus au moyen d'une burette jusqu'au virage au pourpre; la molarité est donnée par la formule:

$$N'_n = \frac{V_c \cdot N'_c}{2.5}$$

où $V_c$ = nombre de ml de solution de chélate utilisés et $N_c$ = molarité de la solution de chélate.

### MODE OPÉRATOIRE

On pèse un poids $p$ de dioxime* qu'on place dans une fiole d'Erlenmeyer et on ajoute 50 ml d'ammoniaque; on porte à très légère ébullition puis ajoute 25 ml mesurés exactement de solution $M/5$ d'acétate de nickel; après quelques minutes d'ébullition on laisse reposer pendant une heure, on transvase dans une fiole de 250 ml en rinçant soigneusement à l'eau distillée et complète jusqu'au trait de jauge. On filtre sur papier ou sur creuset et prélève 25 ml avec une pipette; on ajoute environ 0.3 g de murexide à 1% et coule le chélate disodique au moyen d'une burette jusqu'à fin de virage au pourpre.

L'indimole de *vic*-dioxime[13b] ou nombre de mmoles de *vic*-dioxime contenu dans 100 g de substance est calculé au moyen de la formule:

$$D_x = \frac{V \cdot 200}{p}$$

où $V = (25 \cdot N'_n) - (10 \cdot N'_c \cdot V')$, $V'$ = nombre de ml de chélate $M/50$, $N'_n$ = molarité de la solution d'acétate de nickel et $N'_c$ = molarité de la solution de chélate.

Le titre % en *vic*-dioxime peut être établi au moyen de la formule:

$$T = \frac{D_x \cdot M_T}{1000}$$

où $M_T$ = masse moléculaire calculée de la dioxime essayée.

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* On calcule $p$ de façon à consommer 40 à 50% de nickel.

## RÉSULTATS OBTENUS

La présente methode a été expérimentée sur quelques *vic*-dioximes soigneusement recristallisées; le Tableau I indique les résultats que nous avons obtenus.

TABLEAU I

| *Echantillons dosés* | *Poids utilisé* | *Indimole théorique* | *Indimole trouvé* | *Titre trouvé* |
|---|---|---|---|---|
| Diméthylglyoxime | 0.487 | 861 | 854 | 99.2 |
| | 0.492 | 861 | 856 | 99.4 |
| | 0.508 | 861 | 859 | 99.8 |
| | 0.502 | 861 | 853 | 99.1 |
| Méthyléthylglyoxime | 0.572 | 768 | 771 | 100.4 |
| | 0.580 | 768 | 765 | 99.6 |
| | 0.564 | 768 | 770 | 100.3 |
| | 0.575 | 768 | 765 | 99.6 |
| Cyclohexane-1,2-dione-dioxime (nioxime) | 0.634 | 703 | 705 | 100.3 |
| | 0.642 | 703 | 707 | 100.5 |
| | 0.638 | 703 | 704 | 100.2 |
| | 0.650 | 703 | 701 | 99.7 |
| Di-furilglyoxime (furildioxime) | 0.907 | 450 | 454 | 100.8 |
| | 0.918 | 450 | 451 | 100.2 |
| | 0.952 | 450 | 451 | 100.2 |
| | 0.930 | 450 | 453 | 100.6 |
| Diphénylglyoxime (benzyldioxime) | 1.140 | 416 | 412 | 99.1 |
| | 1.134 | 416 | 412 | 99.1 |
| | 1.142 | 416 | 415 | 99.8 |
| | 1.158 | 416 | 413 | 99.3 |

## RÉSUMÉ

Les *vic*-dioximes peuvent être dosées facilement par précipitation au moyen d'un sel de nickel dont on mesure l'excès volumétriquement par chélatométrie.

## SUMMARY

*Vic*-dioximes can be easily determined by precipitation with a nickel salt, excess of which is titrated with EDTA.

## ZUSAMMENFASSUNG

Die quantitative Bestimmung von *vic*-Dioximen kann durch Fällung mit einer gemessenen Menge Nickelsalzlösung erfolgen, deren Überschuss mit EDTA titriert wird.

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*Anal. Chim. Acta*, 25 (1961) 150–152

# A NEW REAGENT FOR THE DETECTION AND GRAVIMETRIC DETERMINATION OF SODIUM

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(Received January 23rd, 1961)

## INTRODUCTION

With the exception of the triple uranyl acetate salts there are few satisfactory weighing forms for sodium. Other inorganic reagents have been recommended, but these have never been able to compete with the uranyl acetate reagents. In the field of organic reagents, dihydroxytartaric acid has received some attention, but the reagent is unstable and its sodium salt is rather too soluble for general application as a weighing form for sodium. Recently, α-methoxyphenylacetic acid[1,2] and the magnesium salt of 8-aminonaphthalene-1-sulphonic acid[3,4] have been recommended for the gravimetric determination of sodium. As these communications were published during the course of the present study[5], which was concerned with the development of organic precipitants for the alkali metals, particularly sodium and potassium, we have felt it appropriate to include our own observations on these reagents.

α-Methoxyphenylacetic acid is not in our experience as sensitive for sodium as is claimed[1]. The lowest concentration of sodium to give a positive test is 3.3 mg of sodium per ml of test solution. This compares very unfavourably with the uranyl acetate reagents. It is, however, more selective than zinc or magnesium uranyl acetate in that quite large concentrations of lithium do not interfere with its use. The precipitate given by this reagent is apparently an acid double salt of composition $C_6H_5CH(OCH_3)$-$COOH \cdot C_6H_5CH(OCH_3)COONa$. Our results on 50-mg amounts of sodium show a negative error of 5–7%, the magnitude of which increases with a decrease in the amount of sodium present. The published procedure[2] involves the use of several different empirical correction factors which are applied in different circumstances; this seriously detracts from the use of the reagent for precise analytical work. We have also found that substitution in the active centre of the molecule of α-methoxyphenylacetic acid leading to compounds such as α-ethoxyphenylacetic acid, α-methoxydiphenylacetic acid, and α-methoxyfurylacetic acid destroys completely the property associated with the parent compound of forming a sparingly soluble sodium salt[5].

The work of DRANITSKAYA[3] on 1-aminonaphthalene-8-sulphonic acid is of greater significance. The magnesium salt of this acid is sufficiently soluble in water to allow the use of a 10% solution as the reagent. A three-fold excess of the reagent is necessary and the sodium salt is precipitated from a solution containing about 50% of ethanol. No details are given of the amounts of sodium determined, although this reagent is later used[4] for the detection of sodium at a limiting dilution of 1 in 4,000, equivalent to a concentration of 0.25 mg of sodium per ml. The reagent can tolerate potassium, ammonium and lithium in amounts up to about four-fold in excess of that of sodium.

Our studies of naphthylaminesulphonic acids have shown that of the common acids only the 1:8-acid has the properties reported by DRANITSKAYA and even this acid relies on a high reagent concentration and the presence of ethanol to precipitate sodium. It is not as sensitive as the uranyl acetate reagents.

### *New reagents examined*

Numerous reports are found in the chemistry of the anthraquinonesulphonic acids of sparingly soluble alkali metal salts, yet no serious attempt has been made to apply the reactions of these acids for the detection and determination of the alkali metals. In a study of the derivatives of anthraquinone which are reported as having sparingly soluble alkali salts, only one compound has been found to have a sodium salt of sufficiently low solubility for possible analytical application. This compound, 5-benzaminoanthraquinone-2-sulphonic acid, was originally prepared by CLAUS[6] in 1882 to characterise 5-aminoanthraquinone-2-sulphonic acid. He remarks that the sodium salt of this benzoyl derivative is very difficultly soluble in water.

We have now examined this compound and its precursor, 5-aminoanthraquinone-2-sulphonic acid, and find that the sodium salt of the latter is extremely soluble in water whereas the salt of the benzoyl derivative is not. Moreover, this low solubility is associated largely with the benzoyl group. Acylation of the amino-acid with acetyl and propionyl chlorides results in compounds with only moderate sensitivities to sodium: the trifluoroacetyl derivative is much more sensitive, but is not as sensitive as the benzoyl derivative. Isomers of 5-benzaminoanthraquinone-2-sulphonic acid have now been prepared and their reactions with sodium are compared by means of sensitivity determinations carried out under similar conditions. The compounds examined are given in Table I. 5-Trifluoroacetylanthraquinone-2-sulphonic acid is included for comparison.

TABLE I

| *Compound* *Anthraquinone* | *Sensitivity to sodium (mg per ml)* | |
|---|---|---|
| | *1-$SO_3H$* | *2-$SO_3H$* |
| 3-Benzamino | not prepared | 15[a] |
| 5-Benzamino | 2 | 0.10 |
| 8-Benzamino | 20 | 12 |
| 5-Trifluoroacetyl | not prepared | 0.30 |

[a] This compound is the only one which shows a greater sensitivity to potassium, namely 2 mg/ml.

Of the five isomeric compounds, only 5-benzaminoanthraquinone-2-sulphonic acid is worthy of further study. When an aqueous ethanolic solution of this acid is added to an aqueous solution of sodium chloride, precipitation of the sodium salt is not instantaneous, even at concentrations as high as 5 mg per ml. Within 10–60 sec, however, depending on the concentration of sodium, precipitation of the shimmering orange-yellow sodium salt begins and continues until all the sodium in the solution has been consumed. Examination of this precipitate has shown it to have the expected molecular formula, $C_{21}H_{12}NO_6SNa$ (by elemental analysis). It is very sparingly soluble in water, almost insoluble in ethanol, and insoluble in ether. On the basis of the molecular formula, it contains 5.358% of sodium.

Determination of the sensitivity of 5-benzaminoanthraquinone-2-sulphonic acid towards the alkali metals and the ammonium ion shows that the reagent, although lacking in selectivity, is extremely sensitive to the sodium ion. In the test procedure used, the reagent can detect 0.005 mg of sodium in a total volume of 2 ml, *i.e.* at a dilution of 1 in 400,000. Results are given in Table II, following the procedure described in the experimental section.

TABLE II

| *Ion* | *Sensitivity (mg/ml of ion present)* |
|---|---|
| $Li^+$ | 0.60 |
| $Na^+$ | 0.0025 |
| $K^+$ | 0.28 |
| $Rb^+$ | 0.10 |
| $Cs^+$ | 0.08 |
| $NH_4^+$ | 0.25 |

TABLE III

| *Sodium taken (mg)* | *Wt. of ppt. (mg)* | *Sodium found (mg)* | *Error %* |
|---|---|---|---|
| 1.40 | 24.5 | 1.32 | —5.7 |
| 2.90 | 52.2 | 2.80 | —3.5 |
| 4.30 | 79.8 | 4.28 | —0.46 |
| 5.70 | 106.5 | 5.71 | +0.17 |
| 8.60 | 160.4 | 8.60 | 0.00 |
| 10.00 | 186.7 | 10.00 | 0.00 |
| 11.50 | 214.2 | 11.48 | —0.17 |
| 14.30 | 268.6 | 14.39 | +0.62 |
| 17.20 | 322.6 | 17.28 | +0.46 |
| 20.20 | 382.1 | 20.45 | +1.24 |
| 22.80 | 426.6 | 22.86 | +0.26 |
| 25.00 | 465.2 | 24.90 | —0.40 |

The data show that the reagent is most sensitive to sodium, the sensitivity then decreasing in the order caesium, rubidium, ammonium, potassium, and lithium. The high sensitivity to sodium indicates that under the experimental conditions the precipitation of sodium must be complete for most practical purposes. Several quantitative experiments were therefore carried out in order to assess the suitability of the reagent for the gravimetric determination of sodium.

The most satisfactory conditions for the precipitation have now been established as (*1*) the presence of an 80–100% excess of the reagent, (*2*) a content of 50% of ethanol in the test solution, and (*3*) a standing time of 30 min for the ageing of the precipitate. The ethanol converts the initial microcrystalline precipitate into fine, easily filtered, crystalline needles. The sodium salt possesses a very favourable gravimetric factor, 0.05358. Table III lists some results obtained following the procedure described in the experimental section.

These results show that the reagent is quite satisfactory for the gravimetric determination of sodium. The relatively high errors in the determination of the lower amounts of sodium are due to the collection of the precipitate in a macro-crucible with consequent lack of precision. For amounts of sodium below 4 mg it would be better to use the techniques of micro-filtration.

The lower sensitivity of the reagent to.potassium might have enabled its application for the determination of sodium in the presence of potassium, provided that most of the latter was removed, for example, as perchlorate. Solutions of sodium ion containing varying amounts of potassium not exceeding a concentration of 0.2 mg of potassium per ml were analysed by the prescribed method. The results obtained were invariably high indicating that co-precipitation or induced precipitation of the potassium salt occurred. No further work on possible separations of sodium from potassium was done.

## EXPERIMENTAL

### *(A) Preparation of reagent*

Anthraquinone-2-sulphonic acid was nitrated according to the method of FIERZ-DAVID[7] to give 5-nitroanthraquinone-2-sulphonic acid in 40% yield. This compound (10 g) was dissolved in the minimum quantity of boiling water and the hot solution was treated with a solution of sodium sulphide (200 ml; 20%) and sodium hydroxide (40 ml; 30%). The mixture was boiled for a few minutes, then cooled and filtered. The residue was dissolved in sufficient hot water and the solution was filtered to remove sulphur. The blood-red filtrate containing the sodium salt of 5-aminoanthraquinone-2-sulphonic acid was treated with concentrated hydrochloric acid (20 ml) which precipitated the free acid as silver-grey spangles. This was filtered off, and purified by re-precipitation from a solution of the sodium salt. (Yield 4.5 g, 50%. No m.p.). 5-Aminoanthraquinone-2-sulphonic acid (3 g) was dissolved in a mixture of pyridine (3 g) and nitrobenzene (15 g) and treated with benzoyl chloride (3 g). The mixture was heated under reflux at 156° for 0.5 h with continuous stirring.

The golden yellow crystalline needles which formed on cooling the mixture were filtered off, drained by suction, and washed with a small quantity of ether. The air-dried material was dissolved in warm ethanol (200 ml; 40%) and the solution was treated with a solution of sodium chloride (20 ml; 6%). The orange-yellow precipitate was filtered off, washed with cold water and suspended in the minimum quantity of hot hydrochloric acid (1 *N*). The salt slowly dissolved and on cooling the solution, the free acid separated as a fine, yellow, crystalline powder. This was filtered off, washed first with a little hydrochloric acid, then with water and finally air-dried. (Yield 2.0 g, 50%. m.p. 162°d).

### *(B) Determination of sensitivity of the reagent towards the alkali metals and ammonium*

#### *Reagent solution*

3% solution of 5-benzaminoanthraquinone-2-sulphonic acid in 50% aqueous ethanol. The solution is filtered and stored in a hard glass bottle. The stored solution reacts slowly with the alkali of the glass to give a precipitate, which must be filtered off before the solution is used. Alternatively, a polyethylene bottle can be used.

#### *Alkali metal solutions*

Solutions containing 1 mg/ml of alkali metal ion were prepared by dissolving the appropriate weight of the pure dry chlorides in water.

#### *Test procedure*

1 ml of the alkali metal solution contained in a small test tube was mixed with 1 ml of the reagent solution. The tube was stoppered and the contents were shaken for

1 min. The tube was set aside for 10 min, and examined for the appearance of a precipitate. The tests were repeated with progressively diluted solutions of each alkali metal until no precipitate was observed after 10 min from the time of mixing the reagent and test solutions.

### *(C) Gravimetric determination of sodium*

*Reagent solution*

As in *(B)*.

*Procedure*

*1–10 mg of sodium.* Pure, dry sodium chloride (or an aliquot of a solution of sodium chloride in water) was transferred to a 50-ml beaker. The salt was dissolved in 5 ml of water (or the solution concentrated or diluted to approximately 5 ml) and 5 ml of ethanol were added, followed by 15 ml of the reagent. The mixture was set aside for 30 min at room temperature and was stirred occasionally during this period. The precipitate was filtered off on a dry, weighed glass filter (porosity 4) and was washed successively with 3 1-ml portions of ethanol, 6 1-ml portions of ethanol saturated with the sodium salt, and finally with 4 1-ml portions of dry diethyl ether. Air was drawn through the precipitate for 5 min and the filter was then placed in a drying oven at 110°–120° and dried to constant weight (a time of about 30 min sufficed).

*10–25 mg of sodium.* The above procedure was used except that a 100-ml beaker was required and the volume for precipitation was increased from 10 ml to 20 ml in a solution approximately 50% with respect to ethanol; 30 ml of reagent were added. The washing and subsequent treatment of the precipitate were as described above. The theoretical factor is applicable. Thus, the percentage of sodium is given by:

$$\frac{\text{Wt. of precipitate (mg)} \cdot 5.358}{\text{Wt. of sample (mg)}}$$

### *(D) Recovery of reagent*

The filtrates and precipitates from each determination were collected in a suitable vessel and sufficient of a solution of sodium chloride was added to precipitate all the excess reagent as the sodium salt. This was filtered off and treated as described in the section above dealing with the purification of the reagent.

## DISCUSSION

5-Benzaminoanthraquinone-2-sulphonic acid is an extremely sensitive reagent for sodium ions. It is eight to ten times more sensitive than the uranyl acetate reagents. However, its lack of selectivity is a serious disadvantage for many analytical purposes. Although it is a satisfactory reagent for sodium, other alkali metals even in small amounts must be absent.

The relationship between molecular structure and precipitation of alkali metal salts is obscure. Of five isomeric compounds, only one exhibits this remarkable behaviour. It is difficult to understand why this particular orientation of substituents in the anthraquinone molecule produces this effect. Steric factors would not seem to be involved, because of the remoteness of the benzamino-group from the active salt-forming sulphonic acid group. The similarity of the compounds containing the benzamino- and trifluoroacetyl groups might indicate an electronic effect associated particularly with the 2:5-substitution. This particular orientation must give rise during salt formation to a crystal lattice of low energy compared with the lattice energies of the salts of the other derivatives. X-ray diffraction patterns have been obtained for the sodium salts of the six compounds listed in Table I. Each compound has a different diffraction pattern, and thus a different crystal structure. There is no evidence from the X-ray investigation that a chemical similarity exists among all six compounds.

In presenting the details of this new reagent, the authors have had to consider whether its possible applications in analysis are sufficient to justify publication; for there would seem to be little purpose in adding yet another useless reagent to the already overburdened literature on the analytical chemistry of the alkali metals. It is felt, however, that the existence of such a sensitive reagent should be made known. There are indications that further studies in the separation of the alkali metals by techniques such as ion-exchange may overcome the difficulties associated with the non-selectivity of the reagent; the accurate determination of sodium in the presence of other alkali metals would then become simple.

## ACKNOWLEDGEMENTS

We are grateful to Prof. R. BELCHER for his interest in this work, and to Mr. R. C. CHIRNSIDE AND Mr. H. P. ROOKSBY, General Electric Company, Wembley, Middlesex for the X-ray diffraction photographs and their analysis. H.S.G. thanks the Government of India and the University of Mysore for provision of a Central Overseas Scholarship.

## SUMMARY

5-Benzaminoanthraquinone-2-sulphonic acid is recommended as a reagent for the precipitation of sodium. It is the most sensitive precipitant for sodium yet proposed, being able to detect 5 $\mu$g of sodium at a limiting dilution of 1 in $4 \cdot 10^5$. The reagent is not selective and is unable to tolerate the presence of the other alkali metals and the ammonium ion. The use of the reagent for the gravimetric determination of 1.40–25.0 mg of sodium is described.

## RÉSUMÉ

Un nouveau réactif, l'acide benzamino-5-anthraquinone sulfonique-2, est proposé pour l'identification et le dosage gravimétrique du sodium. Cette réaction est très sensible, mais pas sélective; les autres métaux alcalins et l'ammonium gênent.

## ZUSAMMENFASSUNG

Als neues, sehr empfindliches Fällungsreagenz für die Bestimmung von Natrium wird die 5-Benzamino-anthrachinon-2-sulfosäure empfohlen. Die anderen Alkalimetalle und Ammonium-Ionen stören und müssen vorher entfernt werden.

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# ANALYSE THERMOGRAVIMÉTRIQUE DE QUINALDATES MÉTALLIQUES

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(Reçu le 5 décembre 1960)

Au cours d'un travail d'ensemble effectué sur les chélates métalliques de l'acide picolique (pyridine 2-carboxylique)[1] nous avons montré l'utilité de l'analyse thermogravimétrique des produits cristallisés pour déterminer la constitution des chélates, leur taux d'hydratation, la stabilité thermique des molécules d'eau fixées, celle des produits anhydres, et les conclusions intéressantes qu'on pouvait en déduire sur la structure des chélates[2,3].

Une étude parallèle a été poursuivie sur les chélates de l'acide quinaldique (quinoléine 2-carboxylique). Les résultats obtenus font l'objet de la présente communication.

## DÉTAILS EXPÉRIMENTAUX

(*1*) *Préparation des quinaldates*: La présente étude est limitée aux cations suivants: alcalino-terreux Mg, Ca, Ba, et cations bipositifs lourds Cu, Pb, Mn, Cd, Hg, Zn, Ni, Co, Fe.

L'acide quinaldique utilisé était un produit commercial que nous avons purifié par recristallisation dans le benzène.

Les quinaldates alcalino-terreux sont préparés par neutralisation de la solution d'acide par le carbonate correspondant.

Les quinaldates de cuivre, plomb, manganèse, cadmium, mercure, zinc, nickel, s'obtiennent facilement par addition d'une solution de quinaldate de sodium à une solution du sel métallique correspondant; leur filtration et leur séchage sont facilités si on opère en milieu acétique et à chaud; par exemple, le quinaldate de nickel préparé dans ces conditions correspond à un hydrate bien défini à 2 molécules d'eau, alors que le mélange des deux solutions neutres à froid conduit sensiblement à un trihydrate dont une molécule d'eau s'élimine progressivement par un séchage prolongé à l'air sur creuset filtrant en donnant le dihydrate stable.

Deux quinaldates de cobalt différents avaient déjà été préparés par DUTT[4]: l'un, de couleur crême, est obtenu en milieu neutre, l'autre, rose-rouge, en milieu acétique. Ces deux composés, nous les avons également obtenus suivant les indications de DUTT. D'autre part, à partir d'une solution de sel de Mohr contenant 1% de chlorhydrate d'hydroxylamine, nous avons préparé deux variétés définies de quinaldates ferreux: (*a*) par addition de 100 ml d'une solution 0.1 *M* d'acide quinaldique à 50 ml d'une solution 0.1 *M* chaude du sel de Mohr, il se forme, après une intense coloration rouge, un précipité rouge qui est rapidement filtré et lavé à chaud; (*b*) en ajoutant à 50 ml de la solution froide 0.1 *M* de sel de Mohr 100 ml d'une solution 0.1 *M* de quinaldate de sodium, on obtient un précipité violet que l'on filtre et lave à froid.

Tous les quinaldates ont été filtrés sur creusets filtrants no. 3 ou 4, lavés et séchés par aspiration d'air un minimum de 24 h.

(2) *Analyse thermogravimétrique*: L'étude a été effectuée à l'aide de la thermobalance de Chevenard, en atmosphère ordinaire, sur un poids initial moyen de 300 mg.

Une perte de poids de 200 mg correspond à 155–156 mm sur le papier photographique. Les taux d'hydratation sont déterminés par mesure, sur la courbe, de la hauteur du premier palier; on calcule le poids correspondant, rapporté au poids total de précipité, pesé dans son creuset avant et après l'opération. Si la perte d'eau ne se manifestait sur la courbe que par une variation de 8 à 10 mm, on effectuait, pour plus de précision, un autre enregistrement, sur un poids plus important, en fixant la température maximum à celle correspondant au produit du palier anhydre.

Nous avons utilisé le même régime de température que pour les picolates: montée linéaire de 3 degrés environ par min, jusqu'à 700° et maintien 2 h à cette température. C'est le même régime thermique qu'ont utilisé BORREL ET PÂRIS[5] pour leur étude des oxinates et des méthyl-2 oxinates[6] et BOCQUET ET PÂRIS[7] pour l'étude des phényl-2 oxinates.

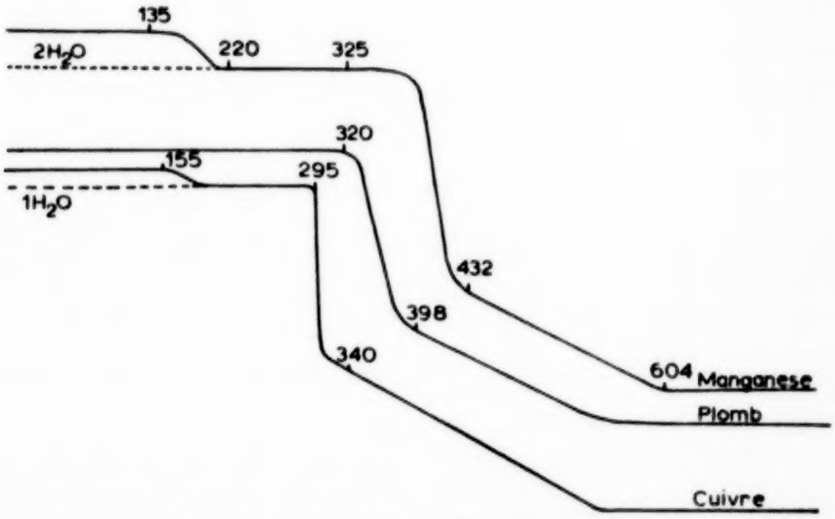


Fig. 1. Thermogravimétrie des quinaldates de cuivre, de manganèse et de plomb.

Les formules des quinaldates sont établies en comparant les pourcentages de métal et d'eau expérimentaux avec les pourcentages théoriques, compte tenu de la nature du résidu: MgO, $BaCO_3$, CaO (dans ce cas, la montée linéaire de 3° par min a été poursuivie jusqu'à 1000°), CuO, PbO, CdO, ZnO, NiO, $Co_3O_4$, $Fe_2O_3$. Dans certains cas, le métal a dû être dosé directement sur le quinaldate après minéralisation: Mg, Mn, Fe, comme il est indiqué sur les Tableaux I et II.

## RÉSULTATS

Nos courbes sont reproduites dans les Figs. 1, 2, 3, et 4. Elles présentent toutes la même allure caractéristique pour la décomposition du chélate, allure que nous avions déjà signalée pour les picolates: perte de poids brutale suivie d'un net changement de pente. Pour les quinaldates de cuivre et de nickel, cette décomposition est même explosive. La décomposition peut conduire au métal, avec les quinaldates de cobalt et nickel (Fig. 3).

Les Tableaux I et II résument les résultats obtenus; $t_1$ est la température de debut de déshydratation du quinaldate, $t_2$ la température de début de décomposition du chélate anhydre. Elles correspondent aux points où la courbe quitte l'horizontale.

En ce qui concerne la composition des différents quinaldates examinés, la littérature fournit plusieurs références sur les quinaldates monohydratés de cuivre[8-14], zinc[8,15-20] et cadmium[12], leur insolubilité permettant de les utiliser pour le dosage de ces cations, seuls, ou en présence d'autres ions dans des conditions déterminées.

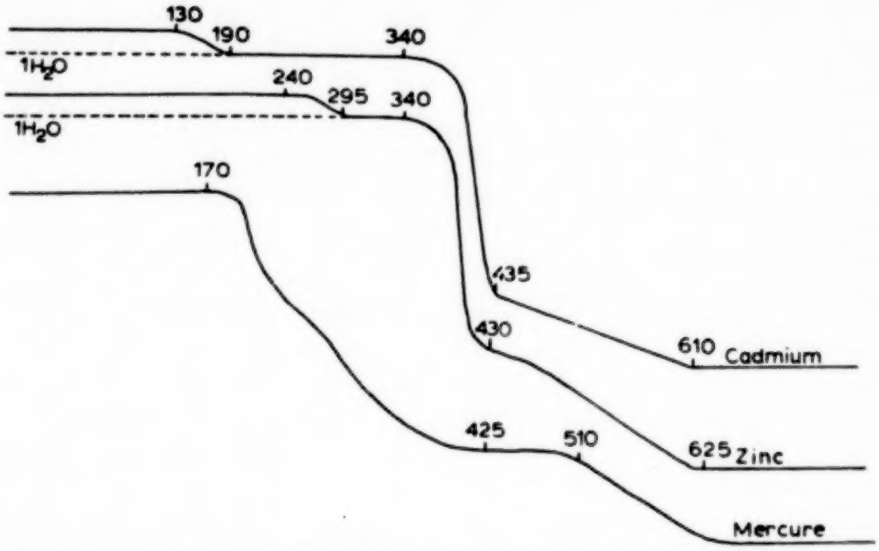


Fig. 2. Thermogravimétrie des quinaldates de cadmium, de zinc et de mercure.

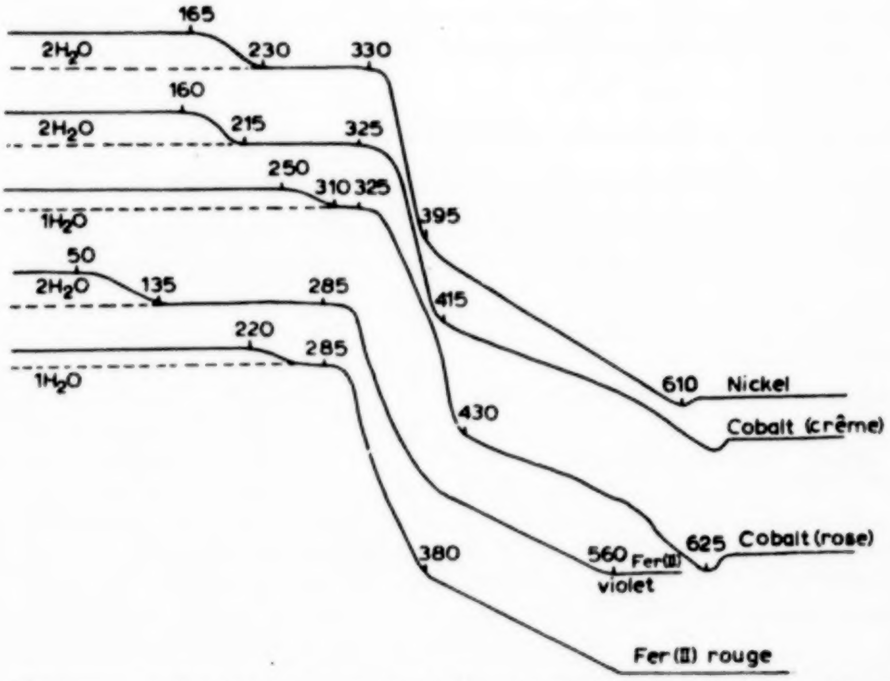


Fig. 3. Thermogravimétrie des quinaldates de nickel, de cobalt et de fer(II).

Les quinaldates de cobalt crême et rose-rouge préparés par DUTT[4] sont décrits avec, respectivement 2 et 0 molécules d'eau, alors que nos résultats conduisent à 2 et 1 $H_2O$, cette molécule d'eau étant particulièrement solide (250°).

Le quinaldate ferreux violet, préparé par RÂY ET BOSE[19] est décrit avec 5 $H_2O$. Celui que nous avons préparé contient 2 $H_2O$. Quant à la variété rouge que nous avons obtenue, sa composition correspondrait à $Fe(C_{10}H_6O_2N)_2 \cdot H_2O$, cette molécule d'eau étant également très solide (220°):

% théoriques pour $Fe(C_{10}H_6O_2N)_2H_2O$; C : 57.44, H : 3.12, N : 6.70, Fe : 13.35.

trouvé; C : 57.38, H : 3.39, N : 6.50, Fe 13.37.

Au cours de la rédaction de cet article, nous avons eu connaissance du résumé d'un travail de LUMME[21] concernant l'étude de la stabilité thermique des quinaldates des cations bipositifs Cd, Co, Cu, Zn, Ni, Pb. Nous avons noté quelques divergences avec nos propres résultats, en particulier au sujet du nombre de molécules d'eau d'hydratation des chélates de nickel (l'auteur signale un trihydrate et un monohydrate) et de zinc (l'auteur signale un tétrahydrate).

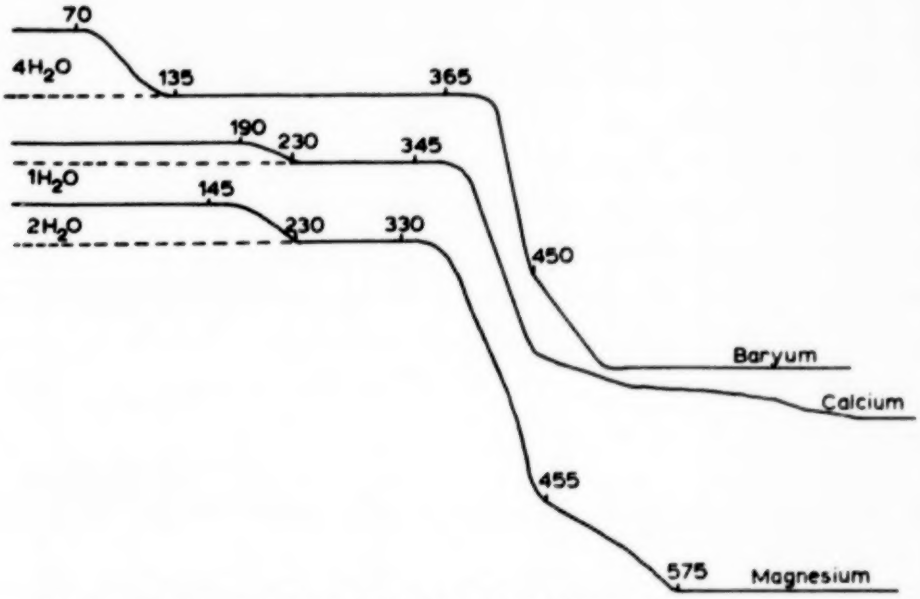


Fig. 4. Thermogravimétrie des quinaldates alcalino-terreux.

TABLEAU I

QUINALDATES DE CATIONS ALCALINO-TERREUX

| *Quinaldate* | *Couleur* | $t_1$ | $t_2$ | *% métal* | | *% $H_2O$* | |
|---|---|---|---|---|---|---|---|
| | | | | *expér.* | *théor.* | *expér.* | *théor.* |
| $Mg(C_{10}H_6O_2N)_2 \cdot 2H_2O$ | blanc | 145 | | 6.14[a] | 6.01 | 8.7 | 8.90 |
| $Mg(C_{10}H_6O_2N)_2$ | | | 330 | 6.50 | 6.60 | | |
| $Ca(C_{10}H_6O_2N)_2 \cdot H_2O$ | blanc | 190 | | 10.04[b] | 9.96 | 4.55 | 4.47 |
| $Ca(C_{10}H_6O_2N)_2$ | | | 345 | 10.52 | 10.42 | | |
| $Ba(C_{10}H_6O_2N)_2 \cdot 4H_2O$ | blanc | 70 | | 24.65[c] | 24.81 | 13.2 | 13.01 |
| $Ba(C_{10}H_6O_2N)_2$ | | | 365 | 28.40 | 28.51 | | |

[a] Dosé sur le quinaldate après minéralisation par le complexon III.
[b] Calculé d'après le résidu CaO obtenu par chauffage a 1000°.
[c] Calculé d'après le résidu $BaCO_3$.

## CONCLUSIONS

### (*1*) *Stabilité thermique des quinaldinates anhydres*

Nous avons représenté sur la Fig. 5 les températures $t_2$ de début de décomposition des quinaldates anhydres, données dans les Tableaux I et II ainsi que les températures correspondantes des oxinates[5] et des picolates[1]. Nous constatons que les stabilités thermiques sont du même ordre de grandeur, les quinaldates ayant, en général, une stabilité intermédiaire entre celles de l'oxinate et du picolate correspondants. En outre, la variation de $t_2$ en fonction de la nature de cation donne pour les 3 réactifs des séries sensiblement parallèles, les quinaldates se situant entre les oxinates et les picolates. Comme l'avaient noté BOCQUET ET PÂRIS[7]: l'ordre des stabilités thermiques est l'inverse de l'ordre des stabilités ioniques.

TABLEAU II

QUINALDATES DE CATIONS BIPOSITIFS LOURDS

| *Quinaldate* | *Couleur* | $t_1$ | $t_2$ | % *métal* |  | % $H_2O$ |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | *expér.* | *théor.* | *expér.* | *théor.* |
| $Cu(C_{10}H_6O_2N)_2 \cdot H_2O$ | bleu-vert | 155 |  | 14.88 | 14.92 | 4.25 | 4.23 |
| $Cu(C_{10}H_6O_2N)_2$ |  |  | 295 | 15.55 | 15.58 |  |  |
| $Pb(C_{10}H_6O_2N)_2$ | blanc |  | 320 | 37.55 | 37.57 |  |  |
| $Mn(C_{10}H_6O_2N)_2 \cdot 2H_2O$ | blanc jaunâtre | 135 |  | 12.74[a] | 12.62 | 8.2 | 8.27 |
| $Mn(C_{10}H_6O_2N)_2$ |  |  | 325 | 13.87[a] | 13.75 |  |  |
| $Cd(C_{10}H_6O_2N)_2 \cdot H_2O$ | blanc | 130 |  | 23.54 | 23.67 | 4.0 | 3.80 |
| $Cd(C_{10}H_6O_2N)_2$ |  |  | 340 | 24.65 | 24.61 |  |  |
| $Hg(C_{10}H_6O_2N)_2$ | blanc |  | 170 |  |  |  |  |
| $Zn(C_{10}H_6O_2N)_2 \cdot H_2O$ | blanc | 240 |  | 15.28 | 15.29 | 4.4 | 4.21 |
| $Zn(C_{10}H_6O_2N)_2$ |  |  | 340 | 15.98 | 15.95 |  |  |
| $Ni(C_{10}H_6O_2N)_2 \cdot 2H_2O$ | vert-bleu | 165 |  | 13.47 | 13.37 | 8.36 | 8.20 |
| $Ni(C_{10}H_6O_2N)_2$ |  |  | 330 | 14.70 | 14.56 |  |  |
| $Co(C_{10}H_6O_2N)_2 \cdot 2H_2O$ | crême | 160 |  | 13.40 | 13.42 | 8.35 | 8.20 |
| $Co(C_{10}H_6O_2N)_2$ |  |  | 325 | 14.60 | 14.61 |  |  |
| $Co(C_{10}H_6O_2N)_2 \cdot H_2O$ | rose rouge | 250 |  | 13.93 | 13.99 | 4.25 | 4.28 |
| $Co(C_{10}H_6O_2N)_2$ |  |  | 325 | 14.55 | 14.61 |  |  |
| $Fe(C_{10}H_6O_2N)_2 \cdot 2H_2O$ | violet | 50 | 285 | 12.76[a] | 12.80 | 8.4 | 8.26 |
| $Fe(C_{10}H_6O_2N)_2$ |  |  |  | 13.94 | 13.95 |  |  |
| $Fe(C_{10}H_6O_2N)_2 \cdot H_2O$ | rouge | 220 | 285 | 13.37[a] | 13.35 | 4.4 | 4.30 |

[a] Dosages effectués sur le chélate après minéralisation, dosage du manganèse par le complexon III et du fer par le bichromate.

## (2) *Nombre et stabilité des molécules d'eau dans les quinaldates cristallisés*

Nous avons rassemblé dans le Tableau III le nombre de molécules d'eau, et les températures de déshydratation correspondantes des chélates de l'acide quinaldique, de l'acide picolique, et de l'oxine.

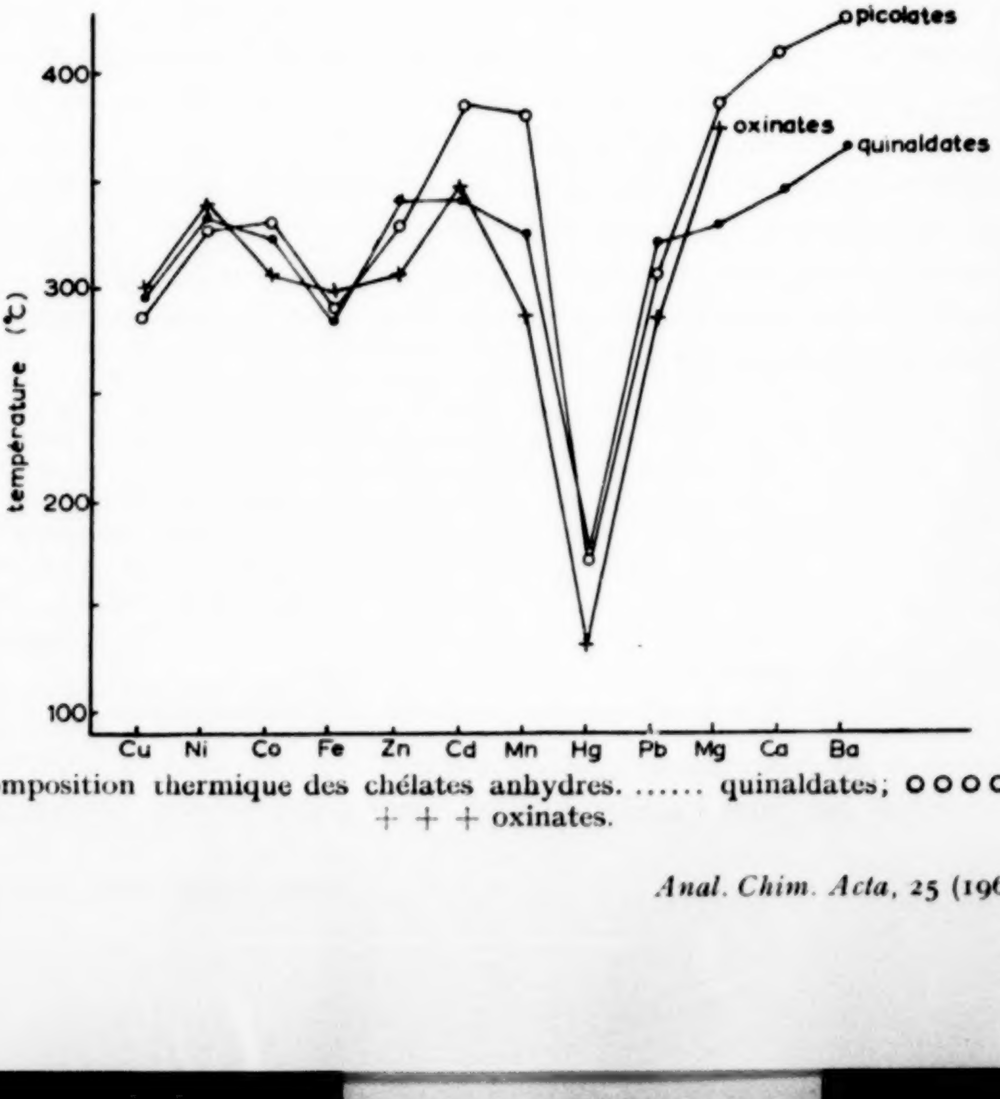


Fig. 5. Décomposition thermique des chélates anhydres. …… quinaldates; O O O O picolates; + + + oxinates.

Dans notre étude antérieure sur les picolates métalliques[1,3] nous avions déduit, de l'examen de la stabilité des molécules d'eau d'hydratation des picolates et des oxinates, une structure possible pour les chélates cristallisés: 2 molécules d'agent chélatant fixées sur un ion métallique bipositif satisfont une coordinence de 4. Si deux molécules d'eau restent également fixées sur le cation, donc solidement, la coordinence est 6 et la structure probable octaédrique; si les molécules fixées le sont faiblement, on peut avancer l'hypothèse d'une coordination limitée à 4.

TABLEAU III

NOMBRE DE MOLÉCULES D'EAU DES CHÉLATES

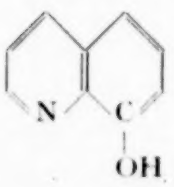
| | *Cd* | *Hg* | *Cu* | *Pb* | *Zn* | *Mn* | *Ni* | *Co* | *Fe* | *Mg* | *Ca* | *Ba* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Quinaldate | 1<br>130 | 0 | 1<br>155 | 0 | 1<br>240 | 2<br>135 | 2<br>165 | 2<br>160<br>1<br>250 | 2<br>50<br>1<br>220 | 2<br>145 | 1<br>190 | 4<br>70 |
| Picolate | 0 | 0 | 2<br>50 | 2<br>50 | 4<br>70 | 2<br>100 | 4<br>75–145 | 4<br>75–145 | 4<br>75–145 | 2<br>145 | 1<br>155 | 0 |
| Oxinate | 2<br>116 | 0 | 2<br>60 | 0–2<br>45 | 2<br>70 | 2<br>117 | 2<br>120 | 2<br>115 | | 2<br>122 | | |
| Méthyl-oxinate | 0 | 1 | 1<br>112 | 1.3<br>45 | 1<br>128 | 1<br>125 | 1<br>215 | 1<br>152 | | 1<br>134 | | |

Si nous comparons les résultats obtenus pour les quinaldates avec ceux précédemment obtenus pour les picolates et oxinates, nous constatons:

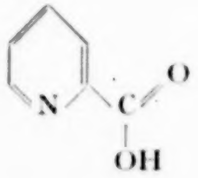
*Les quinaldates de plomb et mercure* sont anhydres; on pourrait leur attribuer une structure tétraédrique comme aux picolates et aux oxinates qui sont soit anhydres, soit hydratés à 2 molécules d'eau faiblement liées.

*Les quinaldates de manganèse, nickel, cobalt, magnésium* ont deux molécules d'eau solidement fixées, comme les oxinates correspondants et comme les picolates, si on ne considère comme solides que les molécules d'eau qui s'éliminent au dessus de 100°; on peut donc, pour les quinaldates de ces cations, envisager une structure octaédrique, comme pour les autres chélates examinés.

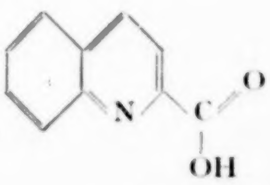
*Les picolates de cuivre, zinc* n'ont que deux molécules d'eau faiblement liées; celui de cadmium est anhydre. Or, les quinaldates correspondants ont tous une molécule d'eau, molécule qui est particulièrement solide. Il nous semble difficile dans ce cas, de faire des déductions valables concernant les structures à partir de ces seuls résultats d'analyse thermogravimétrique.



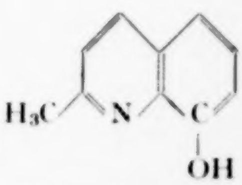
Oxine



Acide picolique



Acide quinaldique



Méthyl 2-oxine

L'environnement du groupement chélatant dans la molécule de l'acide quinaldique est plus encombré que pour l'acide picolique, ou l'oxine. Si nous reportons (Tableau

III) les hydrates des méthyloxinates, à titre de comparaison, nous constatons que ceux de cuivre et de zinc en particulier n'ont qu'une molécule d'eau, et que celle-ci est également solide. Nous pouvons penser que la présence d'une seule molécule d'eau d'hydratation dans ces chélates résulte d'un empêchement stérique.

Il serait naturellement nécessaire de déterminer de façon précise la structure de ces chélates hydratés par une analyse complète du cristal aux rayons X afin de connaître la position exacte des molécules d'eau dans le réseau. Nous ferons simplement remarquer pour l'instant que, lorsque ces structures seront connues, elles devront obligatoirement rendre compte de la solidité des molécules d'eau que notre analyse thermogravimétrique a permis d'établir de façon indiscutable.

## RÉSUMÉ

Les auteurs déterminent par analyse thermogravimétrique le taux d'hydratation, la stabilité thermique des quinaldates anhydres, et la stabilité des molécules d'eau d'hydratation; des déductions possibles sont tirées en relation avec la structure, et par comparaison avec les résultats obtenus antérieurement avec les oxinates et picolates métalliques.

## SUMMARY

Thermogravimetric analysis is used to determine the hydration of metallic quinaldates, as well as the thermal stability of the anhydrous quinaldates and of the water of hydration. Deductions are made with regard to structure by comparison with results previously obtained for oxinates and picolates.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Hydrate von Metallchinaldaten, thermische Stabilität der wasserfreien Chinaldaten und des Hydratwassers durch thermogravimetrische Analyse. Es werden Rückschlüsse auf die Struktur gezogen durch Vergleich mit den Oxinaten und Picolaten.

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# A SENSITIVE NEW METHOD FOR THE DETERMINATION OF NITRITES AND NITROGEN DIOXIDE WITH 4-AMINOAZOBENZENE-1-NAPHTHYLAMINE

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(Received December 7th, 1960)

## INTRODUCTION

In previous work it has been shown that the di-cationic salts of N,N-dimethyl-*p*-(*p*-phenylazophenylazo)aniline type compounds are dark blue with a molar absorptivity of over 100,000 in strongly acid solution[1]. Because of this easily visible color and the high order of sensitivity, analytical methods forming the same type of chromogen were developed for the detection and determination of aniline, naphthylamine and anthramine derivatives, as well as their N-alkyl and N,N-dialkyl analogues[2]. However, unlike the aniline derivatives, 1-naphthylamines reacted readily with the reagent, 4-azobenzenediazonium fluoborate, at room temperature to give the intensely colored chromogen in practically quantitative yield. Hence it appeared that 4-aminoazobenzene and a 1-naphthylamine derivative would react readily with nitrous acid to give the intensely blue di-cation.

The determination of the nitrite ion through formation of an azo dye is a well-known method which has been recently reviewed[3]. The main advantage of the present procedure is its greater sensitivity.

The blue chromogen formed is the dication of 4-(*p*-phenylazophenylazo)-1-naphthylamine. It has a molar absorptivity of 93,000. This value compares favorably with the value of 95,000 obtained in the determination of 1-naphthylamine with 4-azobenzenediazonium fluoborate[2].

## EXPERIMENTAL

*Reagents and equipment.* 4-Aminoazobenzene and 1-naphthylamine (both from Distillation Products Industries) were crystallized several times from pentane to give products melting at 130° and 50°, respectively.

*Reagent solution.* A solution of 0.02 g of 1-naphthylamine and 0.12 g of 4-aminoazobenzene in 40 ml of 2-methoxyethanol was diluted to 100 ml with water.

A Cary Model 11 recording spectrophotometer with 1-cm cells was used in the colorimetric determination.

### *Procedure I*

The residue to be analyzed is dissolved in 5 ml of reagent solution diluted with 5 ml of water. To this solution of sample and reagent is added 1 drop (0.03 ml) of concentrated hydrochloric acid. After 30 min hydrogen chloride gas is passed through for 5 min. During this latter process the temperature of the solution in the water-cooled tube rises from about 26° to about 84° in 2 min and then drops to approximately 44° at the end of the 5-min period. No precautions are taken to keep the temperature constant, as reproducible results are obtained without doing so. The mixture is then cooled to room temperature and diluted to 15 ml with 2-methoxyethanol. The absorbance of the solution at 643 mμ is then determined against a proper blank.

### *Procedure II*

For the collection of nitrogen dioxide, air can be aspirated through 5 ml of 0.02 *N* sodium hydroxide solution, as described by JACOBS AND HOCHHEISER[4]. (In the presence of a large excess of sulfite ion one drop of 1% hydrogen peroxide is added, followed by a 5-min wait). 5 ml of the reagent solution is then added, followed by 2 drops (0.06 ml) of concentrated hydrochloric acid. The mixture is allowed to stand for 30 min. Then hydrogen chloride gas is passed through for 5 min. The mixture is cooled to room temperature and then diluted to 15 ml with approximately 6 *N* hydrochloric acid. The absorbance of the solution at 643 mμ is then determined against a proper blank.

## DISCUSSION

Variables in *procedure I* were investigated. Holding all factors constant except the variable under study, 5 ml of a 0.000162% aqueous solution of sodium nitrite was analyzed. Increasing the concentration of 4-aminoazobenzene in the reagent solution increased the intensity (Fig. 1), which reached a maximum with 0.006 g of this amine per 5 ml of reagent solution. Any greater concentration caused precipitation in the final colored solution. On the other hand a decrease in the amount of 1-naphthylamine in the reagent solution caused a slight increase in intensity throughout the range of amine concentrations investigated (Fig. 2). Use of 0.001 g of 1-naphthylamine per 5 ml of reagent solution gave optimum results; lower concentrations produced about the same intensity, but the higher concentration was preferred so

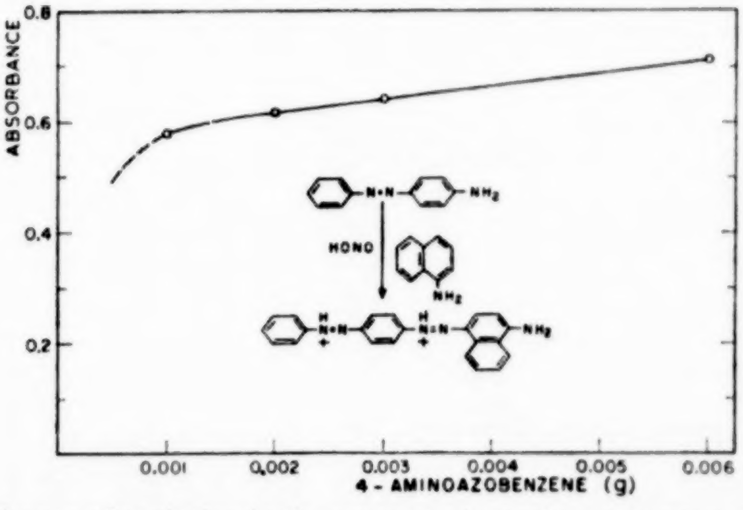

Fig. 1. Effect on absorbance of variation in the amount of 4-aminoazobenzene in 5 ml of the reagent solution containing 1 mg of 1-naphthylamine.

that larger quantities of nitrogen dioxide or nitrite ion could be handled. 1 drop (0.03 ml) of concentrated hydrochloric acid was found to speed up the reaction, but more acid gave no further improvement. A wait of 30 min gave optimum results. After waiting periods of 5 and 120 min, intensities were 2% and 10% lower than the optimum. Passage of hydrogen chloride gas through the solution was found necessary to obtain an essentially quantitative reaction, while passages of 3, 5 and 10 min gave exactly the same intensity. Final dilution of the solution with approximately 6 *N* hydrochloric acid instead of 2-methoxyethanol did not alter the absorbance of the solution. The color intensity was stable for at least 4 h; after 46 h the absorbance had dropped from an initial value of 1.10 to 0.52. For *procedures I* and *II*, Beer's law was obeyed from 0.5 to over 16 $\mu$g of nitrite ion per 15 ml of final solution (Fig. 3).

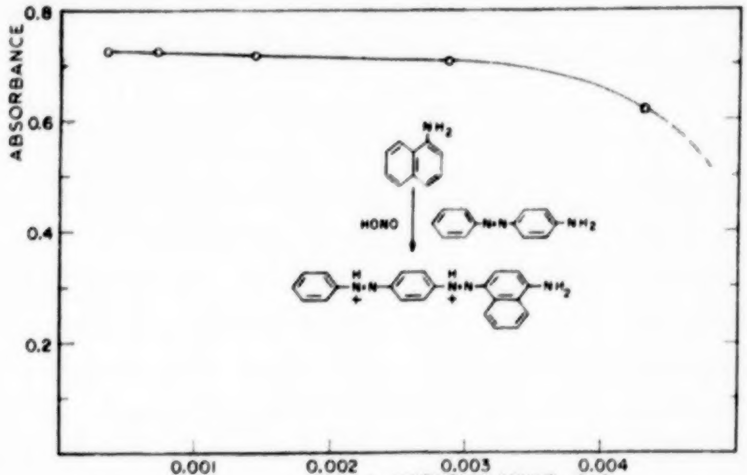

Fig. 2. Effect on absorbance of variation of 1-naphthylamine in 5 ml of the reagent solution containing 6 mg of 4-aminoazobenzene.

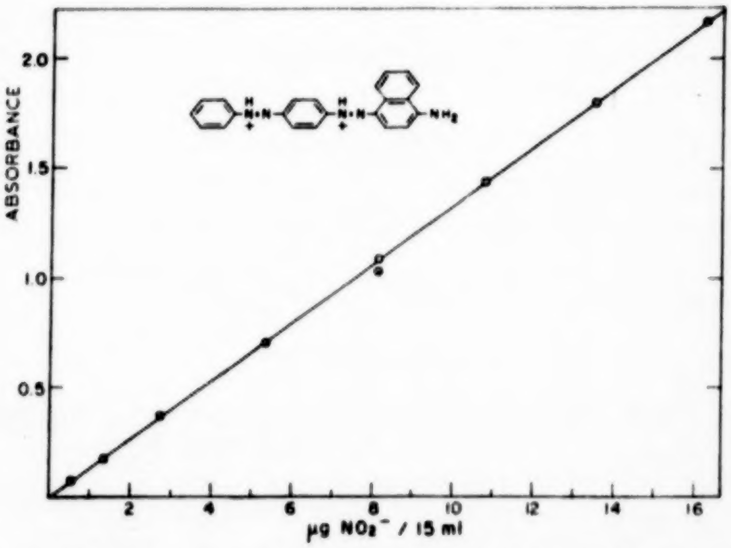

Fig. 3. Concentration–absorbance curve obtained in the spectrophotometric determination of nitrite ion.

N-methyl-1-naphthylamine and N-1-naphthylethylenediamine can be substituted for 1-naphthylamine.

Possible interferences were investigated. The nitrate ion, phenol, nitromethane, formaldehyde, acetone and aromatic nitroso compounds, such as nitrosobenzene and

N,N-dimethyl-*p*-nitrosoaniline gave no blue color in the procedure when they were substituted for the nitrite ion. Nitrate, sulfate and chloride ion did not interfere with the determination of nitrite. To test the interference of sulfur dioxide or the sulfite ion, aqueous solutions of sodium metabisulfite were used. A concentration of the sulfite ion (or sulfur dioxide) twice that of the nitrite ion showed very little interference. However, in the presence of 35 times the concentration of sulfur dioxide the intensity obtained by both procedures was approximately halved. The sulfite ion probably interferes by reducing the diazonium salt formed from nitrous acid and 4-aminoazobenzene to a hydrazine which does not react with 1-naphthylamine to form the blue chromogen. However, as JACOBS AND HOCHHEISER[4] have pointed out, this interference can be eliminated with the use of hydrogen peroxide, as shown in *procedure II*. In the case of a residue containing large amounts of sulfite, *procedure II* can be used by dissolving the residue in 5 ml of 0.02 *N* sodium hydroxide solution followed by treatment with a drop of 1% hydrogen peroxide, etc. With this procedure the interference of sulfite is eliminated to some extent.

## SUMMARY

A sensitive method for the determination of nitrites is proposed. The method should also be applicable to the determination of nitrogen dioxide. The test consists of the reaction of 4-amino azobenzene and 1-naphthylamine with nitrous acid to form the blue di-cation of 4-(*p*-phenylazophenylazo)-1-naphthylamine. Beer's law was obeyed from 0.5 to over 15 μg of nitrite ion per 15 ml of final solution. Spectrophotometrically it is possible to detect 1 part of nitrite ion in 60 million parts of solution.

## RÉSUMÉ

Une méthode sensible est proposée pour le dosage colorimétrique des nitrites et du bioxyde d'azote. Elle est basée sur la coloration bleue, obtenue avec l'amino-4-azobenzène et l'α-naphtylamine.

## ZUSAMMENFASSUNG

Beschreibung einer empfindlichen colorimetrischen Methode zur Bestimmung von Nitriten und Stickstoffdioxyd. Sie beruht auf der Bildung einer blauen Färbung mit 4-Aminoazobenzol und α-Naphtylamin.

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# A MODIFIED TRITIUM GAS COUNTING PROCEDURE

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(Received January 1st, 1961)

The one-step method for tritium analysis[1] has been reported to give a high precision in counting reproducibility. The procedure consists in the quantitative conversion of tritium in organic compounds to a mixture of hydrogen and methane which is then expanded into an ionization chamber and the ion-current measured with a vibrating reed electrometer[2]. Previous experience[3,4] with the technique has proved that it is very satisfactory although some research workers have observed difficulty in the quantitative conversion of some organic compounds, particularly some halogenated derivatives[2,5].

The method of analysis can be divided into four operations:

(*a*) Weighing the sample in solid or liquid form.

(*b*) Conversion of the tritium in the sample into the gaseous state by combustion at approximately 640–675° in the presence of nickelic oxide and zinc catalysts.

(*c*) Introduction of a definite aliquot of this gas into an ionization chamber, followed by dilution to approximately one atmosphere with counting gas such as methane.

(*d*) Measurement of the ion current and therefore the activity in the chamber by means of a vibrating reed-recorder combination.

The error in the first operation can be minimized to less than 0.5% by using a micro-balance whilst that involved in the third and fourth operations is also less than 0.5%[6]. The accuracy of the analysis depends, therefore, to a large extent on the second operation and in this respect the nature of the zinc and nickelic oxide catalysts is of critical importance. Difficulty in obtaining satisfactory results with imported catalysts*, particularly zinc mesh, has prompted us to make a re-investigation of certain aspects of the procedure, particularly the possibility of using very active zinc dust instead of zinc mesh for the combustion.

It is the purpose of this paper to report the results of our investigation into the factors affecting the conversion so as to provide a modified method of high reproducibility. Such factors governing completeness of conversion include: (*1*) the surface area of the zinc; (*2*) absorption of the converted gases by the zinc and nickelic oxide; (*3*) temperature dependence of the diffusion of converted gases through the special glass combustion tube.

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* WILZBACH *et al.*[2] stress the need to use zinc catalyst to the following specifications: "Baker's Analyzed" Blue Label 40 mesh, low in Pb and Fe. This gives satisfactory results but, unfortunately, only 20 mesh was available and this latter catalyst is not satisfactory as the results in this paper show.

## EXPERIMENTAL

### *Materials used*

*Zinc (type 1)*, granular, 20 mesh, Baker & Adamson, low in Pb and Fe. *Zinc (type 2)*, zinc dust, superfine, kept under nitrogen and supplied by By-products & Chemicals Pty. Ltd., Sydney. *Nickelic oxide*, Baker & Adamson, black powder, nickel content 73%. *Combustion glass tubing*, special Pyrex 1720 glass, 1.3 cm I.D. and 1.8 cm O.D., from Corning Glass Works, N.Y. (U.S.A.). *Propane*, 99% purity obtained from Commonwealth Industrial Gases Ltd., Sydney. *t-Benzoic acid*, this was prepared using the Wilzbach technique[7] by exposing 1 g of benzoic acid to 1 C of tritium gas for several weeks. The benzoic acid was recrystallized to radiochemical purity using methanol-water solvent systems. *t-Anthranilic acid*, anthranilic acid (0.5 g) was exposed to 3 C of tritium for two weeks. An aliquot (0.03 g) of this labelled anthranilic acid was diluted with carrier (1.0 g) and recrystallized from hot water to constant activity. In this step traces of phenolic materials could only be removed by alternately using small amounts of charcoal and activated aluminium oxide (Alumina Grade "H", Hopkin & Williams Ltd., England) in the recrystallizing solvent. Distribution experiments (Garnett and Law[8]) with this *t*-anthranilic acid confirmed radiochemical purity.

### *Counting equipment*

Vibrating Reed Electrometer, Cary Model 31, from the Applied Physics Corporation, California (U.S.A.) with the attached multiple leak resistor holder Model 309 and 250-$cm^3$ Borkowski type ionization chambers.

### *Sampling techniques*

*Solids*. Solid samples (approx. 5 mg) were weighed by difference in zinc boats (pressed from pure zinc sheet) using a microbalance to an accuracy of 0.002 mg.

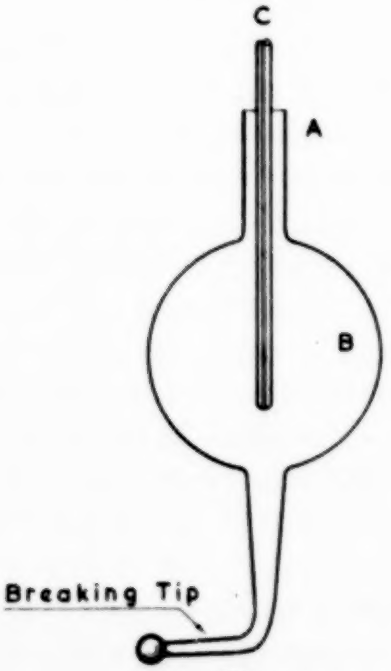

Fig. 1.

*Liquids*. Considerable time was spent in testing various alternatives for liquid sampling. In the original tritium analytical publication[2], sampling was achieved by warming the carrier glass ampoule and allowing the sample to be sucked in as the ampoule cooled. The ampoule was then sealed and the sample weighed by difference. For studies utilizing a system of solvents, particularly volatile solvents (*e.g.* radiometric titrations[9,10]), evaporation caused by the hot glass ampoule introduces an appreciable error. The following procedure was found to give improved accuracy.

A glass ampoule as shown in Fig. 1 was made small enough to be placed in the combustion tube yet possessing a bulb B which was large enough to prevent creep of the liquid sample up the end A. The liquid sample was introduced by capillary C, the end A sealed and sample weighed by difference.

### *Analytical procedure*

The published method[2] was followed as closely as possible. Variations in combustion procedure such as catalyst concentration, temperature, etc., are indicated in the pertinent tables. In general, samples were mixed with zinc and nickelic oxide catalysts in a special combustion tube fitted with a break-seal tip. The reaction tube was then constricted, evacuated to a pressure of less than 0.5 mm, sealed off and combusted in a furnace at approximately 640–675° for the required time (usually 1 h). Oven calibration was performed using a thermocouple which was standardized by C.S.I.R.O. National Standards Laboratory, Sydney. This indicated that the temperature gradient was less than 5° from one end to the other. After cooling to room temperature, the gases in the combustion tube were expanded into a 250-$cm^3$ ion chamber which was then filled to one atmosphere with the counting gas, propane. Propane was used in this step due to the difficulty in obtaining adequate supplies of the recommended methane. The ion current in the chamber was measured by the technique of rate-of-charge of the capacitor rather than by the constant leak circuit which was not quite as accurate for the range of activities measured.

## RESULTS AND DISCUSSION

In Table I, Series A, the effect of the surface area of the zinc on the conversion reaction using *t*-benzoic acid is reported. It can be seen that there is a marked increase in specific activity when the surface area of the zinc is increased. In those samples where granulated zinc was used, incomplete conversion was obtained. Reproducibility in triplicate samples using zinc dust was 2%, so that for the remainder of the studies reported in this paper, zinc dust was used* (*i.e.* Tables II and III).

From the data in Series B of the same table, it can be seen that there is both a decrease in the specific activity and overall reproducibility of the analysis as the proportion of nickelic oxide increases. This can be attributed to either absorption of the converted gases by the nickelic oxide catalyst surface or to a decrease in conversion efficiency of the zinc dust due to the dilution effect of excess nickelic oxide, although from our present evidence this second alternative appears to be unlikely.

The effect of varying the quantity of zinc dust used is reported in Series C. Below 0.5 g of zinc dust (for 0.1 g nickelic oxide) the conversion reaction is incomplete after combustion for three hours. For quantities of zinc dust in excess of this amount, there

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* As these studies were being completed, SWAIN *et al.*[5] also reported the necessity to use zinc dust instead of granulated zinc to obtain complete conversion. However, these authors did not report a detailed study of the analytical procedure using zinc dust catalyst at that time.

## TABLE I

VARIATION IN CATALYST CONDITIONS[a]

| Series | Purpose of experiment | Zinc mesh | Zinc wt(g) | Nickelic oxide (g) | Sample size[b] (mg) | Specific activity (V/min/mg) | Difference in three samples (%) | Remarks |
|---|---|---|---|---|---|---|---|---|
| A | Effect of Zn surface area | 20 | 1 | 0.1 | 2–5 | 0.051[c] | | incomplete conversion |
| | | 20 | 2 | 0.1 | 2–5 | 0.070 | 10 | |
| | | dust | 1 | 0.1 | 2–3 | 0.303 | 2 | |
| B | Variation in quantity of nickelic oxide | dust | 1 | 0.1 | 3–5 | 0.303 | 1.3 | 7.1% decrease in activity/g $NiO_2$ |
| | | dust | 1 | 0.5 | 3–5 | 0.295 | 1.6 | |
| | | dust | 1 | 1.0 | 3–5 | 0.282 | 2 | |
| C | Variation in quantity of zinc | dust | 0.1 | 0.1 | 3–4 | 0.83 | 3 | 3.3% decrease in activity/g Zn |
| | | dust | 0.5 | 0.1 | 2–4 | 1.20 | 2 | |
| | | dust | 1.5 | 0.1 | 2–4 | 1.16 | 2 | |

[a] All combustions were performed at 640 ± 10° for 3 h using 5–6 mg of carrier water per analysis. Evidence for choosing this temperature is shown in Table II.

[b] *t*-Benzoic acid was used for Series A and B, whilst *t*-anthranilic acid was used for Series C.

[c] This figure was the average value of ten samples varying from 0.028 to 0.059 V/min/mg.

## TABLE II

EFFECT OF TEMPERATURE AND TIME OF COMBUSTION[a]

| Wt. of zinc | Wt. of $NiO_2$(g) | Sample size(mg) | Wt. of $H_2O$(mg) | Temp. (± 10°) | Time (h) | Spec. act. (V/min/mg) | %Difference in duplicate | Remarks |
|---|---|---|---|---|---|---|---|---|
| 0.5 | 0.1 | 2–3 | 5–6 | 640 | 0.5 | 0.86 | 3 | Incomplete conversion |
| 0.5 | 0.1 | 2–3 | 5–6 | 640 | 1 | 1.20 | 2 | Complete conversion and no diffusion |
| 0.5 | 0.1 | 2–4 | 5–6 | 640 | 3 | 1.20 | 2 | |
| 0.5 | 0.1 | 2–3 | 5–6 | 640 | 5 | 1.20 | 1.7 | |
| 0.5 | 0.1 | 2–3 | 5–6 | 640 | 16 | 1.20 | 1.8 | |
| 0.5 | 0.1 | 2–3 | 5–6 | 690 | 10 | 1.14 | 0.5 | 0.36% diffusion/h |
| 0.5 | 0.1 | 2–3 | 5–6 | 730 | 11 | 1.14 | 1.5 | 0.4% diffusion/h |

[a] Data in this table are referred to as Series D in the text.

is a slight decrease in specific activity from 1.20 to 1.16 V/min/mg. The value of 1.20 V/min/mg is considered to be a reference figure as data in Table II indicate. The authenticity of this reference value is also confirmed by the activity balance obtained from distribution experiments with anthranilic acid and its brominated derivatives[8]. The observed difference in specific activity can probably be attributed to absorption of tritium on to the catalyst surface. Since this effect was small (3%) for a large increase in zinc dust (300%), this variable was not investigated in further detail and for subsequent analyses (Tables II and III) a catalyst ratio of 5 parts of zinc dust to 1 part of nickelic oxide was used.

From the results in Table II, Series D, it is clear that complete conversion was obtained when a sample of size 2–4 mg was combusted at 640 ± 10° for 1 h. These conditions are ideal for general analysis; however, if the temperature is raised at 690° or above, diffusion of the tritium through the pyrex tubes begins to occur.

The results of experiments designed to examine the remaining variables in the analytical procedure, *e.g.* sample size and carrier water are reported in Table III. The data indicates that when 0.2 g of zinc dust and 0.04 g of nickelic oxide are used per mg of sample the technique is applicable to sample sizes of up to 8 mg and a better precision in duplicate is obtained. Provided that sufficient zinc dust is present, the method seems to be indifferent to the amount of water carrier used. If no carrier is used, the results are low and the same effect is observed if the ratio of water carrier to zinc is very large, as the last analysis in Table III shows. An interesting observation emerges from this series of analyses and this concerns samples which are analysed several days after combustion. Under these conditions, results are usually 3–4% low probably due to the slow absorption of tritium on to the walls of the reaction tube. This discrepancy can be eliminated if the tubes are reheated to 640° for 10 min before analysis.

TABLE III

EFFECT OF SAMPLE SIZE AND WATER CARRIER[a]

| *Series* | *Purpose of investigation* | *Sample (mg)* | *Zinc (g)* | *Nickelic oxide (g)* | *$H_2O$ (mg)* | *Specific activity (V/min/mg)* |
|---|---|---|---|---|---|---|
| E | Variation in sample size | $1.24_3$ | 0.25 | 0.05 | 5–6 | 1.18 |
| | | $2.84_1$ | 0.57 | 0.11 | 5–6 | 1.20 |
| | | $5.06_8$ | 1.01 | 0.20 | 10–11 | 1.20 |
| | | $7.92_8$ | 1.59 | 0.32 | 15–16 | 1.20 |
| F | Variation in water carrier | $2.84_1$ | 0.57 | 0.11 | 5–6 | 1.20 |
| | | $2.40_9$ | 0.48 | 0.096 | 10–11 | 1.19 |
| | | $3.12_8$ | 0.65 | 0.13 | 15–16 | 1.20 |
| | | $2.19_4$ | 0.44 | 0.09 | 20–21 | 1.18 |

[a] All combustions were performed at 640 ± 10° for 1 h.

## *Suggested analytical method*

From the results of this paper, the following conversion procedure is suggested for reproducibility of 0.5%. Zinc dust (0.2 g) and nickelic oxide (0.04 g) per mg of sample is added to the reaction tube with water carrier (5–10 mg), the tube evacuated, sealed and heated at 640 ± 10° for 1 h.

This method has proved satisfactory for the analysis of tritium in the following compounds: anthranilic acid, benzoic acid, cholesterol, 2,4,6-tribromoaniline, 3,5-dibromoanthranilic acid, 5-bromoanthranilic acid, myoinositol, phthalic acid, octanol and octyl phthalate. Details of the analytical data associated with these compounds will be published with each individual project as it is completed.

## ACKNOWLEDGEMENTS

The authors wish to thank the Monsanto Chemical Company (Dr. L. Gruen), the Divisions of Entomology (Dr. D. F. Waterhouse) and Protein Chemistry (Dr. F. G. Lennox) of the Commonwealth Scientific and Industrial Research Organization for grants towards the purchase of the tritium counter and tritium gas. One of us (S. W. LAW) also wishes to acknowledge financial support from the N.S.W. State Cancer Council.

## SUMMARY

The WILZBACH one-step method for tritium analysis has been re-investigated because of difficulty in obtaining satisfactory results with the available catalysts. The important factors governing the conversion of tritium from an organic compound to the gaseous phase have been studied. Such factors include the use of zinc dust instead of zinc mesh for the reduction step, temperature of combustion, and the effect of variation in catalyst weight and sample size on conversion efficiency.

## RÉSUMÉ

Les auteurs ont effectué une étude au sujet de la méthode de WILZBACH pour l'analyse du tritium par comptage; ils ont examiné les différents facteurs intervenant dans la formation du tritium gazeux, à partir de composés organiques.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die WILZBACH'sche Methode zur Bestimmung von Tritium nach dem Zählverfahren unter besonderer Berücksichtigung der Faktoren, welche die Überführung organisch gebundenen Tritiums in gasförmiges Tritium beeinflussen (Reduktionsmittel, Verbrennungstemperatur, Katalysator).

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# *p*-(3-HYDROXY-3-PHENYLTRIAZENO)-PHENYLTRIMETHYL-AMMONIUM CHLORIDE AS A NEW COLOUR REAGENT FOR CERTAIN METAL IONS

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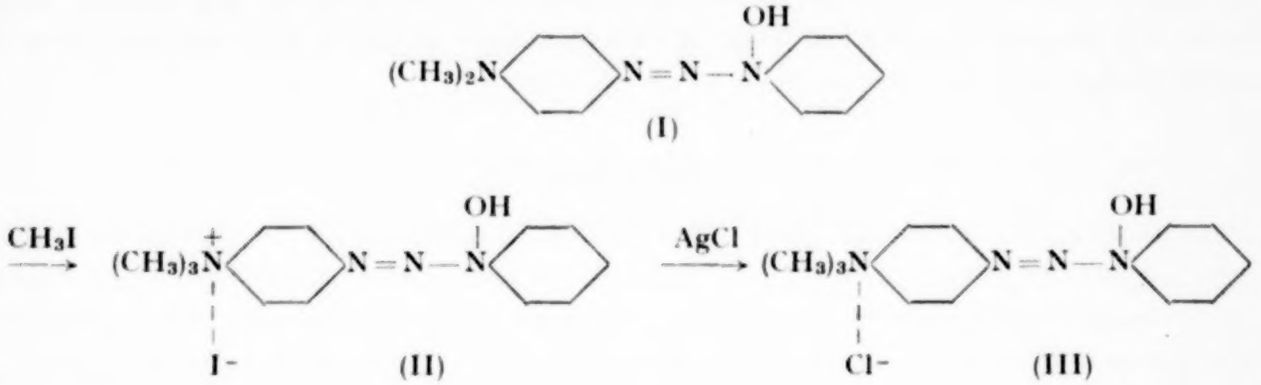
(Received November 22nd, 1960)

Water solubility is generally regarded as a desirable characteristic of organic reagents used in colorimetric analysis. In order to fulfil this condition, certain polar groups such as sulfonic acid, carboxylic acid or hydroxyl groups are introduced into the organic reagent in addition to the usual chelating groups. YOE[1], KLOOSTER[2], and EPHRAIM[3] have studied the effect of introducing such solubilising groups and have shown that the introduction of such groups does not appreciably affect the properties of the complex-forming groups, but yields water-soluble inner complex anions rather than the usual insoluble inner complex precipitate with metal ions. In certain cases the selectivity and specificity of the reagent for certain metal ions is also increased by the introduction of such groups.

In organic chemistry, an excellent example of solubilisation is found in the case of high molecular ketonic compounds (steroids) which can be converted into water-soluble hydrazone derivatives with GIRARD reagent[4]. The presence of the highly polar quarternary ammonium group makes these compounds soluble and water extractable. In the present investigation an attempt has been made to prepare a new colorimetric reagent which is a derivative of the already known 3-hydroxy-1,3-diphenyltriazene proposed by SOGANI AND BHATTACHARYA[5] as a reagent for palladium and other metal ions; these authors used the sulphonic acid derivative[6] of the parent compound as a colorimetric reagent. However, the solubilising action of the trimethyl-ammonium chloride group is greater than that of acidic groups, hence it could be expected that *p*-(3-hydroxy-3-phenyltriazeno)-phenyltrimethylammonium chloride would be more useful and also free from any interference which could be caused by the acidic groups in the analysis of cations. The present paper deals with the synthesis and qualitative reactions of the reagent. Spectrophotometric and quantitative studies of the reagent are still under investigation.

## PREPARATION AND PROPERTIES OF THE REAGENT

The method used for the synthesis of the reagent was SOGANI AND BHATTACHARYA'S[5] modification of BAMBERGER'S method[7]. Diazotised *p*-aminodimethylaniline was coupled with phenylhydroxylamine to give 1(*p*-dimethyl-amino-phenyl)-3 phenyl-3 hydroxy-triazene (I). This compound was converted to corresponding quarternary ammonium iodide (II) by mixing the dried product with excess of methyl iodide. After about 48 h, the precipitated quarternary ammonium iodide was filtered and shaken with excess of freshly precipitated silver chloride suspension in water. The silver iodide precipitate and excess of silver chloride were filtered off and the required reagent (III) was obtained on evaporating the filtrate.



(I) (II) (III)

The composition of the product was checked by determining the nitrogen and the ionic chlorine contents. (Found: N = 18.01, Cl = 11.71. Calc. for $C_{15}H_{19}N_4OCl$: N = 18.27, Cl = 11.91). The reagent is yellowish green in colour; it shows no sharp m.p. but starts decomposing at about 180°.

### REACTIONS WITH VARIOUS METAL IONS

Before the colorimetric determination of any metal ion was studied with the proposed reagent, qualitative tests were carried out by conventional procedures. A 1.0% solution of the reagent was prepared in distilled water and the reagent was added dropwise to about 0.5 ml of 1.0% salt solutions (usually chlorides) till the intensity of the colour was a maximum. The pH adjustments were made with *N* hydrochloric acid and 10% w/v sodium acetate, indicator paper or a pH meter being employed. The formation of the characteristic colour was observed both in the cold and on heating.

The colour reactions of the various metal ions with the reagent are summarised in Table I.

TABLE I

| *Metal ion* | *Optimum pH of the reaction* | *Colour of the complex* | *Sensitivity of the reaction (µg)* | *Remarks* |
|---|---|---|---|---|
| $Ni^{+2}$ | 5.0–6.5 | Bright yellow | 0.08 | Stable to heat up to 85° |
| $Cu^{+2}$ | 2.0–7.0 | Chocolate brown | 0.60 | Stable to heat up to 80° |
| $Co^{+2}$ | 5.0–7.0 | Dark brown | 0.05 | Stable to heat up to 80° |
| $Mn^{+2}$ | 5.5–7.0 | Brown | — | Unstable to heat. N.Q.* |
| $Cd^{+2}$, $Zn^{+2}$, $Pb^{+2}$ | Neutral | Light yellow | 0.05 | Unstable to heat. N.Q.* |
| $Fe^{+2}$, $Fe^{+3}$ | 3.0–4.5 | Greenish blue | 0.50 | Unstable to heat. N.Q.* |
| $V^{+4}$ | 1.5–3.5 | Light green | 0.50 | Unstable to heat. N.Q.* |
| $Ti^{+4}$ | 1.5–3.5 | Orange | 0.50 | Unstable to heat. N.Q.* |
| $Pd^{+2}$ | 1.5–7.0 | Yellowish brown | 0.85 | Stable to heat up to 90° |
| $Hg^{+2}$ | 4.0–7.0 | Yellow | — | Unstable to heat |
| $Ag^{+}$ | 4.0–7.0 | Yellow | — | Reduced to metallic state |

* N.Q. = not quantitative

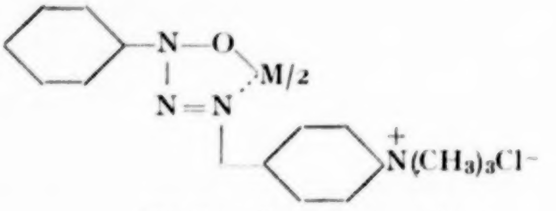
In the case of silver and lead, the ionic chloride of the reagent first precipitated the respective halides. With an excess of lead, the salt formed a yellow colour while silver was reduced to metallic state.

### EFFECT OF NEUTRAL SALTS AND INTERFERING ACID RADICALS

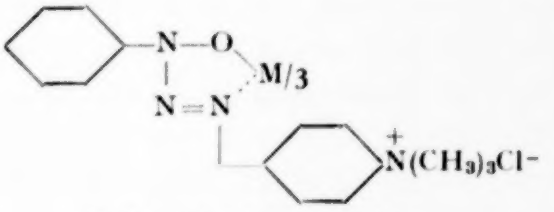
In most cases the colour of the complex was not affected by the presence of indifferent metal ions (chlorides, sulphates and nitrates of alkali and alkaline earth metals) up to a concentration of 10 to 15%. The acid radicals also have no appreciable effect because the complex formation takes place in acidic medium, but the reactions are masked completely by the presence of cyanide ions.

## DISCUSSION

The quarternary ammonium group can be used satisfactorily to solubilise organic reagents and their metal complexes. The introduction of this group into the molecule of 3-hydroxy-1,3-diphenyltriazene does not affect the complex-forming properties of the group —N=N—N—OH. The metal complexes of the reagent in solution may be represented by the following general formulae



IV (for divalent metals)



V (for trivalent metals)

in which the presence of a polar group prevents the precipitation of the complex.

The introduction of the salt-like group does not interfere with the reactions of the metal ions. The ionisation of the trimethylammonium chloride group is much greater than that of the usual acidic groups such as the sulphonic acid group and the solubilities of the reagent and its metal complexes are therefore also larger. The reagent satisfies the requirements of an ideal colorimetric and complexometric reagent.

## SUMMARY

The synthesis and qualitative reactions of *p*-(3-hydroxy-3-phenyltriazeno)phenyltrimethylammonium chloride are described. The solubilising effect of the quarternary ammonium group is studied; this group is valuable for the conversion of organic precipitants to colorimetric reagents.

## RÉSUMÉ

Le chlorure de *p*-(hydroxy-3-phényltriazéno-3)-phényltriméthylammonium est proposé comme nouveau réactif coloré pour certains cations. L'effet solubilisant du groupe ammonium quaternaire a été examiné.

## ZUSAMMENFASSUNG

Als neues Farbreagenz für eine Anzahl Metallionen wird das *p*-(3-Hydroxy-3-phenyltriazeno)-phenyltrimethylammoniumchlorid empfohlen.

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# THE DETERMINATION OF FLUORIDES IN NATURAL WATERS, WITH PARTICULAR REFERENCE TO SEA WATER

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(Received January 28th, 1961)

Until recently methods for the determination of traces of fluoride in natural waters were almost all based on the ability of the ion to destroy the coloured organic complexes of certain metals, *viz.* zirconium, thorium, titanium, aluminium or ferric iron, through the formation of the very stable complex fluorides of the metals. The decrease in colour of the metal complex is a measure of the fluoride concentration. Beer's law is frequently not obeyed in these procedures owing to the diversity of complex fluorides which can co-exist in the solution.

These methods suffer from the disadvantage that sulphate ion also bleaches the organic complexes owing to the formation of stable complex sulphates, *e.g.* $[ZrO(SO_4)_2]^{-2}$. The interference of sulphate can be reduced in a number of ways. The reaction may be carried out[1,2] in the presence of a great excess of sulphuric acid, which produces a more stable reagent[3], but with a considerable loss in sensitivity. The effect may be compensated[4,5] for by raising the sulphate content of the sample to a constant level by the addition of sodium sulphate. Precipitation of the sulphate with barium ions[6] introduces inaccuracies owing to co-precipitation effects and is tedious. Fluoride can be separated[7] from sulphate in brackish waters by passing the sample through the barium form of a cation exchange resin (Zeocarb 215), but large concentrations of chloride interfere. In a method[8] for the determination of fluoride in drinking water by the zirconium–eriochrome cyanine R complex, the interference of sulphate has been eliminated by a preliminary separation of the fluoride by adsorption on an anion exchange resin. Steam distillation[9,10] of fluoride from perchloric, sulphuric or phosphoric acid[11] medium in the presence of silica, serves to separate the ion from sulphate and most other interfering ions. The process is rather time consuming and requires close control, poor recoveries being obtained at low fluoride levels, particularly in the presence of aluminium.

The high concentration of chloride found in sea and ocean water has a considerable influence on the bleaching action of fluoride on the lake, and tends to cause the latter to precipitate. Since the $SO_4^{-2}$ : $F^-$ ratio of sea water is very high (1500:1) the interference of sulphate is likely to be particularly severe in this medium. For the determination of fluoride in sea water the bleaching of the reddish-violet lake formed between zirconyl ion and alizarin red S has been used[12]. The method is not particularly sensitive, is slow and of poor precision. In order to control sulphate interference ANSELM AND ROBINSON[2] have determined fluoride in sea water using this lake in a sulphuric acid medium. This reduces the sensitivity even further and the reaction requires 6 h to attain equilibrium. MATIDA[13] has applied this procedure to the determination of fluoride in the surface and shallow waters of Tokyo Bay.

Recently, a new spot test for the detection of fluoride ion has been reported[14] and the reaction has been applied[15] to the determination of fluorine in organic compounds. In this test, the fluoride ion reacts with the red cerous chelate of alizarin complexone (1 : 2-dihydroxy-anthraquinonyl-3-methylamine-N:N-diacetic acid); the resultant blue complex apparently contains fluoride and cerium alizarin complexone in a 1 : 1 molar ratio[16]. The reagent of BELCHER *et al.*[14,15] has been applied[17] to the determination of fluoride in deposit gauge samples, after a preliminary separation of interfering cations by ion exchange.

In these laboratories an investigation of the constancy of ionic composition of sea and ocean waters is in progress. It was, therefore, decided to investigate the potentialities of this reagent for the determination of fluoride in sea water.

### *Development of the method*

By simple preliminary tests the sensitivity[18] of the reagent to fluoride was found to be *ca.* 0.004 $\mu$g/cm$^2$.

It has been found[16] that complexes with alizarin complexone are formed by scandium and yttrium and all the lanthanons, and of these only those of lanthanum, cerium, praseodymium, and to a lesser extent samarium, form a fluoride complex. While investigating the possibility of achieving a higher sensitivity by use of other lanthanon elements the above observations were confirmed independently. Thus it was found that lanthanum, cerium, praseodymium, neodymium and samarium formed the fluoride complex (the sensitivity to fluoride falling with increasing atomic number) and terbium, erbium, ytterbium, scandium and yttrium failed to do so. The intermediate elements europium and gadolinium form extremely weakly coloured fluoride complexes. Elements Nos. 61, 66, 67, 69 and 71 were not examined. The wavelengths of the absorption maxima of the various lanthanon – alizarin complexones were not significantly different, neither was there any wavelength shift among the

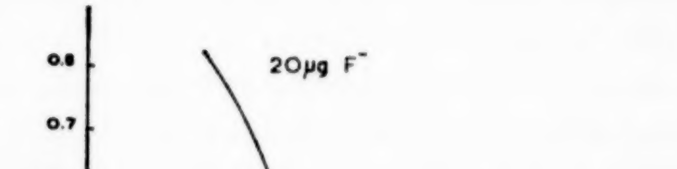

Fig. 1. Optical densities of the fluoride complexes of the chelates of the lanthanons with alizarin complexone as a function of atomic number.

fluoride complexes of the elements from lanthanum to samarium. The results, which are shown in Fig. 1, were obtained by adding 2.0-ml volumes of 0.002 *M* alizarin complexone and 0.004 *M* lanthanon solutions to 20 μg of fluoride in 25-ml graduated flasks containing acetic acid/sodium acetate buffer and 4 ml of acetone (acetone enhances the colour of the fluoride complex; *vide infra*). Twenty minutes after diluting to volume the optical densities of the solutions were measured at 622 mμ in 1-cm cells against a reagent blank. Owing to the greater sensitivity to fluoride shown by lanthanum (Fig. 1) it was decided to use this element in the development of the method.

### *Absorption spectra*

The absorption spectra of the lanthanum–alizarin complexone chelate and its complex with fluoride are shown in Fig. 2. The maximum sensitivity to fluoride is at 622 mμ.

### *Effect of variation of lanthanum concentration*

In a preliminary investigation of the influence of lanthanum concentration upon the fluoride sensitivity and blank, it was found that as its concentration in the final volume was increased above *ca.* 0.0004 *M*, precipitation of the complex occurred. This effect was overcome by stabilising the complex with acetone, sufficient acetone being added to the solutions before addition of the reagents, to make its final concentration not less than 12% vol/vol with respect to acetone. In addition to having a stabilising effect, the presence of acetone increased the sensitivity of the reagent to fluoride by *ca.* 60% (to 0.0018 μg/cm$^2$). The effect of variation of lanthanum concentration in the presence of acetone is shown in Table I. The results were obtained by making additions of 0.004 *M* lanthanum solution to a 25-ml graduated flask containing 25 μg of fluoride, 2.5 ml *M* sodium acetate solution, 2.5 ml *N* acetic acid solution, 4.0 ml acetone and 2.0 ml 0.002 *M* alizarin complexone. They show that the final concentration of lanthanum in the developed solution should be about 0.0003 *M*.

TABLE I

EFFECT OF VARIATION OF LANTHANUM CONCENTRATION UPON OPTICAL DENSITY OF SOLUTIONS

| *ml 0.004 M La* | *O.D. at 622 mμ*[a] | | *Difference* |
|---|---|---|---|
| | *Blank* | *25 μg F$^-$* | |
| 0.0 | 0.028 | 0.028 | — |
| 1.0 | 0.256 | 0.763 | 0.507 |
| 1.5 | 0.296 | 0.870 | 0.574 |
| 2.0 | 0.314 | 0.895 | 0.581 |
| 3.0 | 0.337 | 0.905 | 0.568 |
| 4.0 | 0.348 | 0.900 | 0.552 |

[a] Measured in 1-cm cells

### *Conformity to Beer's law*

Fig. 3 shows the linear relationship, up to *ca.* 25 μg, between the fluoride content and the optical density, and also illustrates the influence of reagent concentration upon the linearity. Curve A was obtained by use of equal volumes (2.0 ml) of 0.002 *M* and 0.004 *M* alizarin complexone and lanthanum respectively, when the relationship is linear up to 20 $\mu$g of fluoride. A 25% increase in the concentration of both reagents produces (curve B) an extension of the linearity to *ca.* 25 $\mu$g.

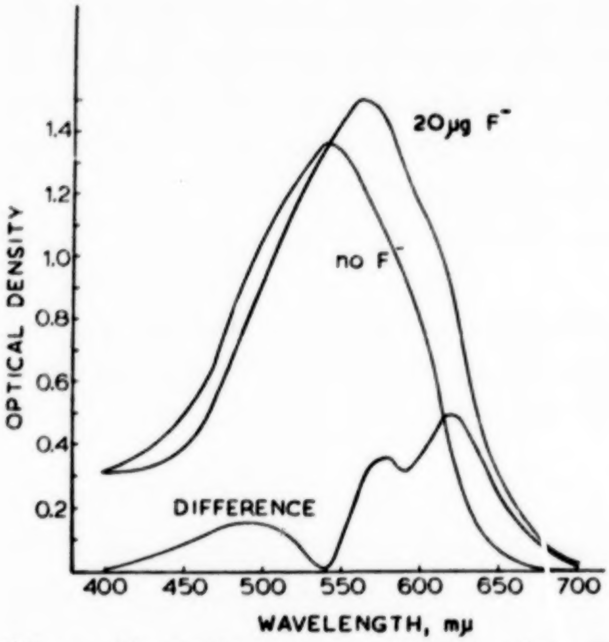

Fig. 2. Absorption curves of the lanthanum–alizarin complexone chelate and its fluoride complex. 1-cm cell; 25-ml volume.

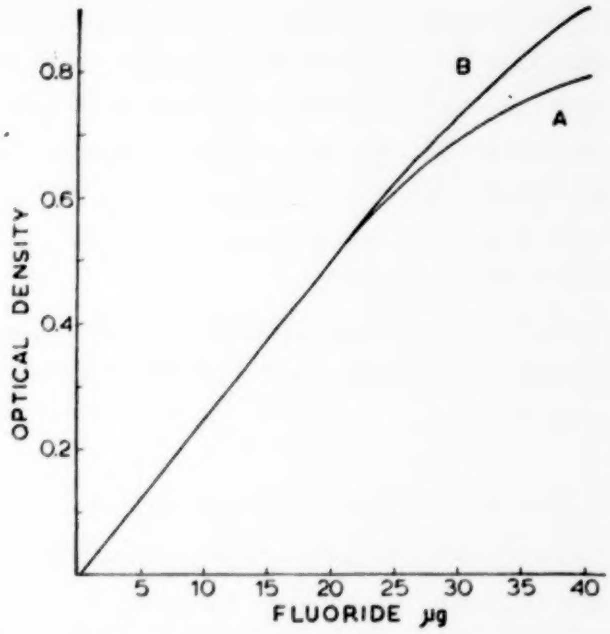

Fig. 3. Calibration curve for fluoride using the lanthanum–alizarin complexone reagent. 1-cm cell, 25-ml volume, 622 m$\mu$. Curve A: 2.0 ml 0.002 *M* alizarin complexone, 2.0 ml 0.004 *M* lanthanum. Curve B: 2.5 ml 0.002 *M* alizarin complexone, 2.5 ml 0.004 *M* lanthanum.

### *Stability of developed coloured complexes*

In non-saline solutions, the colour development of the lanthanum–alizarin complexone and of its fluoride complex was found to be practically instantaneous, and both complexes were remarkably stable, showing little change even after several days. The presence of 15 ml of artificial sea water (prepared as described by LYMAN AND FLEMING[19] from fluoride-free reagents) delayed the development of the maximum colour slightly, but had no effect on its stability.

It was found that the aqueous solutions of alizarin complexone aged, resulting in a decrease in sensitivity to fluoride, thus, the optical density calibration value for 25 $\mu$g of fluoride dropped from 0.585 to 0.528 in a week. Since the colour of the developed reagent blank was known to be exceptionally stable it was decided to prepare a combined reagent containing lanthanum–alizarin complexone, acetone and the buffering components. With this reagent the optical density calibration for 25 $\mu$g of fluoride did not change appreciably in a week.

### *Effect of pH variation*

Aliquots (8.0 ml) of the combined reagent, described below but containing no acetic acid, were added to 25-ml graduated flasks containing 15-ml aliquots of artificial sea water and varying amounts of 6 *M* acetic acid solution. The optical densities were measured and compared with those of identical solutions containing 20 $\mu$g of fluoride. The results shown in Table II indicate that the pH of the solution must be kept within the range 4.45–4.85. Owing to the high acetone content of the solution the pH values shown in Table II must be considered to be only apparent values. It was found that the pH of the buffered solution was slightly lowered by the presence of salts. In order to make the pH values of saline and non-saline solutions the same, a standard amount of dilute acetic acid solution must be added to the reagent blank.

TABLE II

EFFECT OF APPARENT pH UPON THE OPTICAL DENSITIES OF LANTHANUM–ALIZARIN COMPLEXONE AND ITS FLUORIDE COMPLEX

| *ml 6 M acetic acid* | *apparent pH* | *Optical density*[a] | | *Difference* |
|---|---|---|---|---|
| | | *Artificial sea water* | *Artificial sea water + 20 μg $F^-$* | |
| 0 | 6.20 | 0.471 | 0.566 | 0.095 |
| 0.25 | 5.08 | 0.423 | 0.841 | 0.418 |
| 0.30 | 5.02 | 0.421 | 0.850 | 0.429 |
| 0.50 | 4.84 | 0.409 | 0.856 | 0.447 |
| 0.60 | 4.76 | 0.404 | 0.853 | 0.449 |
| 0.70 | 4.69 | 0.394 | 0.842 | 0.448 |
| 0.90 | 4.57 | 0.380 | 0.828 | 0.448 |
| 1.00 | 4.43 | 0.376 | 0.820 | 0.444 |
| 1.25 | 4.32 | 0.354 | 0.791 | 0.437 |
| 1.50 | 4.25 | 0.340 | 0.757 | 0.417 |
| 2.00 | 4.15 | 0.308 | 0.704 | 0.396 |
| 2.50 | 4.04 | 0.275 | 0.651 | 0.376 |
| 3.00 | 3.97 | 0.248 | 0.600 | 0.352 |
| 4.00 | 3.82 | 0.174 | 0.461 | 0.287 |
| 6.00 | 3.71 | 0.122 | 0.322 | 0.200 |

[a] Optical densities measured at 622 mμ in 1-cm cells, against distilled water

### *Method*

Unless otherwise stated, a Unicam S.P. 500 spectrophotometer was employed for all optical density measurements. A slit width of *ca.* 0.05 mm was used. pH measurements were made with a Pye Master pH meter using a glass electrode.

### *Reagents*

(*1*) Combined lanthanum–alizarin complexone reagent. Dissolve 0.0479 g of alizarin complexone in 0.1 ml of concentrated ammonium hydroxide and 1.0 ml of 20% w/v ammonium acetate, together with a few ml of distilled water. Filter the solution through a small Whatman No. 1 paper into a 200-ml graduated flask containing 8.2 g of anhydrous sodium acetate (A.R.), 6.0 ml of glacial acetic acid and sufficient distilled water to dissolve the solids. Wash the filter paper with a small volume of water. Add 100 ml of acetone slowly, with swirling. Dissolve 0.0408 g of lanthanum oxide (spectrographic grade) in 2.5 ml of 2 *M* hydrochloric acid, warming gently to aid dissolution, and mix with the aqueous acetone solution. Dilute to 200 ml with water. Mix well and readjust the volume after about 30 min. The reagent is stable for at least one week.

(*2*) Sodium fluoride solution. Prepare a stock solution containing 1 mg of fluoride/ml by dissolving 2.210 g of sodium fluoride in 50 ml of water containing 1 ml of 0.1 *N* sodium hydroxide and diluting to 1 l. Dilute the stock solution daily to give a working standard containing 10 μg of fluoride/ml.

### *Procedure*

To 15 ml of filtered (Whatman No. 1 paper) sea water, contained in a 25-ml graduated flask, add 8.0 ml of the combined reagent, dilute to volume and mix well. With samples having chlorinities considerably less than 20‰ it is necessary to add also (0.4–0.02 $x$)ml of 6 $N$ acetic acid, where $x$ is the chlorinity of the water. The chlorinity need only be known to the nearest 5 units. A reagent blank is similarly prepared by adding the same volume of the reagent to 15 ml of distilled water containing 0.4 ml of the dilute acetic acid solution.

TABLE III

INTERFERENCE OF ANIONS ON THE DETERMINATION OF FLUORIDE

| *Anion* | *Added as* | *Amount of anion added* | *Optical Density*[a] |
|---|---|---|---|
| None | — | — | 0.497 |
| Borate | $H_3BO_3$ | 0.25 mg | 0.497 |
| Borate | $H_3BO_3$ | 0.50 mg | 0.497 |
| Bromide | KBr | 0.75 mg | 0.498 |
| Bromide | KBr | 1.25 mg | 0.501 |
| Chloride | NaCl | 0.085 g | 0.513 |
| Chloride | NaCl | 0.170 g | 0.513 |
| Chloride | NaCl | 0.255 g | 0.524 |
| Chloride | NaCl | 0.340 g | 0.532 |
| EDTA | disodium salt | 1 ml 0.001 $M$ | 0.444 |
| Iodide | KI | 2 µg | 0.497 |
| Perchlorate | $KClO_4$ | 2 mg | 0.497 |
| Phosphate | $KH_2PO_4$ | 1 µg | 0.496 |
| Phosphate | $KH_2PO_4$ | 10 µg | 0.494 |
| Silicate | $Na_2SiO_3$ | 26 µg | 0.495 |
| Silicate | $Na_2SiO_3$ | 65 µg | 0.498 |
| Silicate | $Na_2SiO_3$ | 5.1 mg | 0.494 |
| Silicate | $Na_2SiO_3$ | 16.5 mg | 0.484 |
| Sulphate | $Na_2SO_4$ | 26.4 mg | 0.492 |
| Sulphate | $Na_2SO_4$ | 52.8 mg | 0.482 |
| Nitrate | $KNO_3$ | 10 µg | 0.495 |
| Nitrite | $NaNO_2$ | 10 µg | 0.496 |

[a] Measured at 622 mµ in 1-cm cells against a reagent blank

The blank and sample solutions, when diluted to volume, should have apparent pH values of 4.50 ± 0.02. Measure the optical density of the sample solution at 622 mµ in a 1-cm cell against the reagent blank after 30 min. Calibrate the method in the same manner using 15-ml aliquots of distilled water containing 1.0, 1.5 and 2 ml of the dilute standard fluoride solution with the addition of 0.4 ml of 6 $N$ acetic acid. For sea waters having chlorinities in the range 15 to 20‰ the observed optical densities of the samples must be multiplied by 1.040 to compensate for salt error. Correction factors at other chlorinities may be interpolated from the data in Table V.

### *Effect of other anions and cations*

The effect of various anions and cations on the determination of 20 µg of fluoride, by the method described above, was investigated. The optical densities measured against a reagent blank, are shown in Tables III and IV respectively. The optical density difference for 20 $\mu$g of fluoride is 0.497.

In these tables the amounts of the various cations or anions under investigation were chosen generally with reference to ocean waters, in which the concentrations of chloride, sulphate, bromide, borate, magnesium and calcium are relatively high. The more reliable estimations of the amount of aluminium in ocean waters indicate that the element is present to the extent of only about 0.01 p.p.m.; at this concentration its interference in the method is negligible. No interference would be anticipated from iron, copper, nickel, cobalt and zinc since their concentrations in sea waters are below 0.1 p.p.m.

TABLE IV

INTERFERENCE OF CATIONS IN THE DETERMINATION OF FLUORIDE

| *Cation* | *Added as* | *Amount of cation added* | *Optical density*[a] |
|---|---|---|---|
| None | — | — | 0.497 |
| Aluminium | $Al\ NH_4(SO_4)_2 \cdot 12\ H_2O$ | 0.5 $\mu$g | 0.492 |
| Aluminium | $Al\ NH_4(SO_4)_2 \cdot 12\ H_2O$ | 1.0 $\mu$g | 0.479 |
| Aluminium | $Al\ NH_4(SO_4)_2 \cdot 12\ H_2O$ | 2.0 $\mu$g | 0.475 |
| Aluminium | $Al\ NH_4(SO_4)_2 \cdot 12\ H_2O$ | 8.0 $\mu$g | 0.415 |
| Barium | $BaCl_2 \cdot 2\ H_2O$ | 2.0 $\mu$g | 0.496 |
| Calcium | $Ca(ClO_4)_2$ | 4.2 mg | 0.494 |
| Calcium | $Ca(ClO_4)_2$ | 8.4 mg | 0.492 |
| Cobalt | $CoCl_2 \cdot 6\ H_2O$ | 10.0 $\mu$g | 0.525 |
| Copper | $CuSO_4 \cdot 5\ H_2O$ | 10.0 $\mu$g | 0.514 |
| Iron | $NH_4\ Fe(SO_4)_2 \cdot 12\ H_2O$ | 1.0 $\mu$g | 0.499 |
| Iron | $NH_4\ Fe(SO_4)_2 \cdot 12\ H_2O$ | 50.0 $\mu$g | 0.478 |
| Magnesium | $Mg(ClO_4)_2$ | 12.7 mg | 0.455 |
| Magnesium | $Mg(ClO_4)_2$ | 25.4 mg | 0.422 |
| Nickel | $Ni(NO_3)_2 \cdot 6\ H_2O$ | 10.0 $\mu$g | 0.520 |
| Uranium | $UO_2(NO_3)_2 \cdot 6\ H_2O$ | 100.0 $\mu$g | 0.497 |
| Uranium | $UO_2(NO_3)_2 \cdot 6\ H_2O$ | 1.0 mg | 0.506 |
| Zinc | $ZnSO_4 \cdot 7\ H_2O$ | 10.0 $\mu$g | 0.500 |

[a] Measured at 622 m$\mu$ in 1-cm cells against a reagent blank

*Application of the method to sea water*

The effect of the salts present in sea water upon the sensitivity of the method to fluoride was determined. Known amounts of fluoride were added to 15-ml aliquots of distilled water and artificial sea waters having chlorinities of 5.05, 10.13, 15.20 and 20.26$^0/_{00}$. These solutions were treated with 8 ml of the mixed reagent and appropriate volumes of 6 $N$ acetic acid to give the solution a pH of 4.50 ± 0.02, when made up to a volume of 25 ml. Optical densities (O.D.) measured against the reagent blanks are shown in Table V.

At each chlorinity, Beer's law is followed closely up to 25 $\mu$g of fluoride. Since the average optical density increments of fluoride are identical at chlorinities 15 and

20°/₀₀, the salt error correction for sea water samples having chlorinities in this range is a constant and equal to +4.0%. From the data in Table IV it appears that most of the salt error is due to magnesium.

*Reproducibility of the method*

Replicate analyses (11) were performed, according to the method, on 15-ml portions of a filtered surface sample (46°30′ N, 8°00′ W) and gave a mean fluoride content of 1.371 µg/ml. The standard deviation was 0.0038 µg/ml and the coefficient of variation 0.28%. The results were obtained by measuring the optical densities, against a reagent blank, with an Optika CF4 spectrophotometer.

TABLE V

THE EFFECT OF SALTS UPON THE FLUORIDE DETERMINATION

| *Fluoride added (µg)* | *Chlorinity of sea water (Cl °/₀₀)* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *0* | | *5.05* | | *10.13* | | *15.20* | | *20.26* | |
| | *O.D*[a] | *O.D/µgF⁻* | *O.D*[a] | *O.D/µgF⁻* | *O.D*[a] | *O.D/µgF⁻* | *O.D*[a] | *O.D/µgF⁻* | *O.D*[a] | *O.D/µgF⁻* |
| 15 | 0.376 | 0.0251 | 0.372 | 0.0248 | 0.368 | 0.0246 | 0.365 | 0.0243 | 0.364 | 0.0243 |
| 18 | 0.447 | 0.0248 | 0.444 | 0.0247 | 0.437 | 0.0243 | 0.432 | 0.0240 | 0.432 | 0.0240 |
| 20 | 0.495 | 0.0247 | 0.487 | 0.0244 | 0.479 | 0.0240 | 0.476 | 0.0238 | 0.475 | 0.0238 |
| 22.5 | 0.556 | 0.0247 | 0.548 | 0.0244 | 0.539 | 0.0240 | 0.533 | 0.0237 | 0.533 | 0.0237 |
| 25.0 | 0.617 | 0.0247 | 0.607 | 0.0243 | 0.598 | 0.0239 | 0.591 | 0.0236 | 0.590 | 0.0236 |
| Average O.D/µg | — | 0.0248 | — | 0.0245 | — | 0.0241 | — | 0.0238 | — | 0.0238 |
| Average salt error | 0 | | −1.2% | | −2.9% | | −4.0% | | −4.0% | |

[a] Optical densities measured at 622 mµ in 1-cm cells against a reagent blank

In order to check the recovery of fluoride from sea water the optical density developed with known amounts of fluoride added to 12.5-ml aliquots of the same sea water were measured, and the fluoride recovery was evaluated from calibration curves

TABLE VI

RECOVERIES OF ADDED FLUORIDE FROM A SEA WATER

| *µg F⁻ added* | *Optical density*[a] *Difference* | *Fluoride (µg) from calibration curve* | *Fluoride (µg) recovery* |
|---|---|---|---|
| 0 | 0.418 | 17.40 | — |
| | 0.419 | | |
| 4.00 | 0.507 | 21.35 | 3.95 |
| | 0.507 | 21.35 | 3.95 |
| | 0.506 | 21.30 | 3.90 |
| 5.00 | 0.531 | 22.40 | 5.00 |
| | 0.531 | 22.40 | 5.00 |
| | 0.531 | 22.40 | 5.00 |
| 6.00 | 0.556 | 23.50 | 6.10 |
| | 0.557 | 23.50 | 6.10 |
| | 0.554 | 23.40 | 6.00 |

[a] Measured at 622 mµ against the reagent blank in 1-cm cells

derived from Table V. The results which are given in Table VI show that the recovery is quantitative and that the average error is $\pm 0.05$ $\mu$g with *ca.* 20 $\mu$g of fluoride.

### *Application of the method to non-saline waters*

The method described for sea waters can be applied directly to the majority of fresh waters without the necessity of applying the salt error correction, since the concentrations in such waters of chloride, sulphate, magnesium and other ions contributing to the salt effect, are negligible.

The most serious interference with the reagent is that of aluminium, which, although it does not react with the alizarin complexone to any appreciable extent, except at high concentrations, forms extremely stable fluoro compounds, particularly $AlF_6^{-3}$, and thereby prevents the reaction of fluoride with the lanthanum-alizarin complexone complex. The effectiveness of any procedure designed to separate aluminium from fluoride, or *vice versa*, is obviously dependent upon the relative molar concentrations of these ions in the solution. An attempt[17] to remove the aluminium from solution, prior to the fluoride determination, by use of a cation exchange resin was not entirely successful, the aluminium-fluoro complexes proving too stable to be broken down by the resin. Incomplete recoveries of micro amounts of fluoride have also been observed[7] when using a strongly basic anion exchange resin as a means of separation from similar concentrations of aluminium. The classical method of separation of fluoride by distillation as a mixture of silicon tetrafluoride and hydrofluoric acid from acid solution is also unsatisfactory in the presence of much aluminium, and the effectiveness of phosphoric acid in the prevention of aluminium interference in this distillation has recently[20] been questioned.

TABLE VII

SEPARATION OF ALUMINIUM FROM FLUORIDE BY CONTINUOUS SOLVENT EXTRACTION AS OXINATE

| *Sample content* | *Optical density*[a] | *$\mu$g $F^-$ recovered* |
|---|---|---|
| 12 $\mu$g $F^-$ standard | 0.294 | 12.0 |
| 12 $\mu$g $F^-$ extracted | 0.293 | 12.0 |
| 12 $\mu$g $F^-$ + 12 $\mu$g $Al^{+3}$ extracted | 0.299 | 12.3 |
| -do- | 0.294 | 12.0 |
| 12 $\mu$g $F^-$ + 12 $\mu$g $Al^{+3}$ without extraction | 0.210 | 8.6 |
| 12 $\mu$g $F^-$ + 120 $\mu$g $Al^{+3}$ extracted[b] | 0.285 | 11.7 |
| -do- | 0.281 | 11.5 |
| -do- | 0.284 | 11.6 |
| 12 $\mu$g $F^-$ + 120.0 $\mu$g $Al^{+3}$ without extraction | Less than reagent blank | 0.0 |

[a] Optical densities measured against a reagent blank

[b] 5.0 ml acetone/oxine used in the extraction, followed by a further 5.0 ml after 20 min

For solutions which contain 2 p.p.m. of aluminium and fluoride the authors have found that complete removal of aluminium as oxinate can be achieved by use of a continuous solvent extraction apparatus[21]. To 20.0 ml of the sample solution in the extractor was added 2.0 ml of 2 *M* sodium acetate solution, 0.45 ml of 6.0 *N* acetic acid solution, and, with mixing, 1.0 ml of a 20% solution of 8-hydroxyquinoline in acetone. After the extraction was completed the aqueous phase was separated from the chloroform contained in the extractor, and filtered through a small filter paper which was washed with water. The combined filtrate and washings were diluted to 50 ml. Water containing 2 p.p.m. of fluoride was treated in the same manner. Aliquots (20 ml) were used for the fluoride determination in each case. The results, together with those obtained at higher aluminium concentrations, are given in Table VII, and show that by this extraction procedure fluoride can be determined in the presence of a forty-fold stoichiometric excess of aluminium. For comparison the optical density differences of the solution without extraction are included in the table. In addition, this extraction procedure will remove many other possible interfering cations, *e.g.* iron(III).

## SUMMARY

The chelate formed between lanthanum and alizarin complexone has been used as the basis of a method for the determination of fluoride in natural waters, with special reference to sea water. The fluoride complex formed with the reagent is developed rapidly at pH 4.50 by the addition of a single buffered reagent and is stable for several days. The fluoride complex is formed in 16% v/v acetone solution; the acetone stabilises the reagent and increases its sensitivity to 0.0018 $\mu$g/cm$^2$. Beer's law is followed up to *ca.* 25 $\mu$g of fluoride. The interference of inorganic ions present in natural waters has been investigated. Abnormally large amounts of aluminium interfere seriously, but can be removed by extraction as its oxinate in a continuous extractor. For sea water of chlorinity within the range 15 to 20‰ the salt error correction is constant and equal to 4.0%. The method showed a coefficient of variation of 0.3% with a sea water containing 1.37 $\mu$g of fluoride/ml.

## RÉSUMÉ

Une nouvelle méthode a été mise au point pour le dosage spectrophotochimique des fluorures dans les eaux, en particulier, dans l'eau de mer. Elle est basée sur la réaction obtenue avec le réactif lanthane–"alizarin complexone" (acide dihydroxy-1,2-anthraquinonyl-3-méthylamine-N,N-diacétique).

## ZUSAMMENFASSUNG

Beschreibung einer neuen Methode zur Bestimmung von Fluorid in Wasser, besonders Meerwasser. Sie beruht auf der Messung der optischen Dichte des Komplexes, der mit Lanthan–Alizarinkomplexon entsteht.

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# DETERMINATION OF SILICA IN IRON ORE

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(Received January 10th, 1961)

The percentage of silica in iron ore is usually determined in the course of a more or less complete analysis, following alkaline fusion. In many instances, the emphasis is on silica alone, and one may prefer a method that gives only the silica content.

We have modified previously known methods for the determination of silica as the sparingly soluble potassium fluosilicate, and have developed a useful titrimetric method for silica in iron ore. The advantages over previously used methods are speed and applicability over the whole range 0.5–20% of silica.

LANGMYHR[1] has shown that silica, hydrofluoric acid and water form a constant-boiling system with the composition 10% hydrofluoric acid, 36% fluosilicic acid and 54% water and with a boiling point of 116° at 1 atm. Below the corresponding concentration of total silica and below this boiling point, there is no loss of silicon on heating; this has been utilized in the procedure described below, where the ore sample is dissolved in a hot mixture of hydrochloric and hydrofluoric acid. The acid mixture also contains potassium chloride, and potassium fluosilicate is formed as the sample dissolves. After cooling, the precipitate is collected on a filter and determined titrimetrically according to the net reaction

$$K_2SiF_6 + 4\,OH^- = Si(OH)_4 + 6\,F^- + 2\,K^+$$

Determination of silica in iron and carbon steel as potassium fluosilicate has been described by KORDON[2] and the method has been extended to alloyed steel by VANDAEL AND JEHENSON[3]. SAJO[4] has described a similar method for ores, slags and ceramics. LANGMYHR's principle of dissolving the sample in a hot mixture of hydrochloric and hydrofluoric acids was not employed by these workers, who all added potassium chloride and hydrofluoric acid to the already dissolved sample.

Our results indicate that calcium interferes in the presence of trivalent iron; SAJO neglects this complication.

The precipitate of potassium fluosilicate may be washed with an ethanolic solution of potassium chloride, as described by SAJO[4] and by MARIMOTO AND MIZUNO[5], but in our opinion an aqueous solution may be used with certain advantage, if the procedure is adjusted accordingly.

## EXPERIMENTAL

### *Procedure*

From a sample of finely ground ore, 0.1–0.4 g is weighed into a 200-ml polytrifluoroethylene beaker. After addition of 15 ml of concentrated hydrochloric acid, 10 ml of 1 : 1 hydrofluoric acid and 5 ml of 20% potassium chloride solution, the beaker is placed on a boiling water-bath for 1 h. After 30 min, the ferric iron is reduced by addition of saturated aqueous stannous chloride solution; 1 ml usually suffices. After complete reaction, the solution is diluted with 15 ml of distilled water and the beaker is cooled for about 15 min in cold water.

The precipitate formed is collected on a cellulose filter pad, placed on a polyethylene sieve disc in a polyethylene funnel. The filtrate is collected in a plastic beaker. The precipitate is washed with cold 20% potassium chloride, in 3-ml portions, until *ca.* 20 ml of collected filtrate changes from red to yellow with 2 drops of 0.1 *N* sodium hydroxide and methyl red as indicator. The filter pad with the precipitate is transferred quantitatively to a 400-ml plastic beaker, suspended in *ca.* 100 ml of boiling water and is titrated with 0.1 *N* sodium hydroxide with phenolphthalein as indicator.

## DISCUSSION

If the precipitate is washed with a 5% potassium chloride solution in 50% aqueous ethanol, practically none of the potassium fluosilicate dissolves, and the percentage of silica can be calculated according to theory.

$$\% \ SiO_2 = 0.150 \cdot \text{ml NaOH/g sample}$$

We have found that the procedure recommended here gives reproducible results, but 8.5% of the precipitate dissolves in the wash fluid, and the factor 0.150 must be changed to the empirical factor 0.160, which also corresponds to the blanks in our reagents. Washing with an aqueous solution of potassium salts is also described by KORDON[2] and has the advantage of greater speed over an ethanolic solution. An

TABLE I

| *Sample* | *% $SiO_2$ grav.* | *% $SiO_2$ Volumetric not reduced* | *% $SiO_2$ Volumetric reduced* | *% CaO* |
|---|---|---|---|---|
| Kip-D[5]<br>*ca.* 60% Fe | 3.18 | 3.52 | 3.15 | 6.7 |
| Kip-D[5]<br>*ca.* 60% Fe | 4.23 | 4.42 | 4.21 | 7.5 |

TABLE II

| *Sample* | *% $SiO_2$ grav.* | *% $SiO_2$ volumetric* | *% deviation abs.* | *Spread in parallel runs* |
|---|---|---|---|---|
| Mesabi standard | 2.08 | 2.05<br>2.06 | —0.025 | 0.01 |
| Luossavaara Cl | 3.96 | 3.96<br>3.94 | —0.01 | 0.02 |
| Kiruna B | 2.21 | 2.17<br>2.18 | —0.035 | 0.01 |
| Tuolluvaara A | 3.20 | 3.28<br>3.20 | +0.04 | 0.08 |
| Tuolluvaara Cl | 3.58 | 3.56<br>3.54 | —0.03 | 0.02 |

empirically calibrated method is usually inevitable in routine work, and a simple nomogram can be recommended. The digestion time in the first reaction must not be cut below 60 min, as we have found that the precipitate remains too soluble with shorter reaction times.

TABLE III

| | *Sample* | *Luossavaara D*[a] | *Kiruna D*[a] | *Nimba* |
|---|---|---|---|---|
| % known | $SiO_2$ | 9.30 | 2.69 | 3.52 |
| | $Fe_2O_3$ | 1.9 | 3.0 | 93.8 |
| | $Fe_3O_4$ | 78.2 | 80.9 | — |
| | MnO | 0.1 | 0.1 | 0.1 |
| | CaO | 2.7 | 5.3 | 0.3 |
| | MgO | 1.3 | 0.9 | 1.5 |
| | $Al_2O_3$ | 1.6 | 0.5 | 1.1 |
| | $TiO_2$ | 0.7 | 0.2 | 0.2 |
| | $V_2O_5$ | 0.2 | 0.2 | — |
| | $P_2O_5$ | 0.8 | 4.3 | 0.2 |
| | S | 0.03 | 0.02 | 0.03 |
| | $CO_2$ | 1.2 | 0.4 | — |
| | $Na_2O$ | 0.5 | 0.1 | — |
| | $K_2O$ | 0.5 | 0.3 | — |
| | CuO | 0.02 | 0.04 | — |
| $SiO_2$ % found | 60 min digestion | 9.34 | 2.82 | 3.51 |
| | | 9.25 | 2.88 | 3.50 |
| | | 9.25 | 2.72 | 3.48 |
| | 90 min digestion | 9.43 | 3.04 | 3.64 |
| | | 9.75 | 3.20 | 3.58 |
| | | 9.38 | 3.10 | 3.59 |

TABLE IV

INFLUENCE OF ALUMINIUM AND TITANIUM

| *Added mg $SiO_2$* | *Added mg $Al^{+3}$* | *Added mg $Ti^{+4}$* | *Found mg $SiO_2$* | *Rel. deviation* | |
|---|---|---|---|---|---|
| 16.45 | 5.0 | | 16.60 | +0.9 | 60 min digestion |
| 13.60 | 10.0 | | 13.70 | +0.7 | |
| 14.15 | 15.0 | | 14.65 | +3.5 | |
| 14.10 | | 5.0 | 14.05 | −0.4 | |
| 13.62 | | 10.0 | 13.70 | +0.6 | |
| 14.60 | | 15.0 | 15.20 | +4.1 | |
| 11.05 | 5.0 | | 11.10 | + 0.5 | 90 min digestion |
| 11.90 | 10.0 | | 13.80 | +17.5 | |
| 15.95 | 15.0 | | 19.08 | +19.8 | |
| 12.30 | | 5.0 | 12.30 | ± 0 | |
| 15.40 | | 10.0 | 16.00 | + 3.9 | |
| 13.10 | | 15.0 | 13.95 | + 6.5 | |

The recommended time on the water-bath — 60 min — was also found to be optimal with regard to interferences from other constituents of the ore, especially calcium, aluminium and titanium, which may coprecipitate if too much of the original hydrochloric acid evaporates. The presence of these elements also necessitated the use of hydrochloric acid in the dissolution of the ore; otherwise a combination of hydrofluoric acid and potassium chloride was found to convert the silica to potassium fluosilicate.

The Lappland iron ores contain calcium as apatite, and the combination of trivalent iron and calcium interferes with the determination of silica, unless the iron is reduced, as is shown in Table I.

The method was developed for Kiruna ore, but it was tested on other ores with good results (Table II).

The influence of digestion time is shown in Tables III and IV. In Table III, natural ore samples were used; in Table IV, large amounts of interfering elements were added in synthetic samples. The iron is not reduced to the divalent state.

Aluminium and titanium were found in the final solution after titration. The interference of these two elements through coprecipitation is the most serious limitation of the method. In the filtrate after collection of the potassium fluosilicate, all the iron and phosphorus and probably other minor constituents are available for determination.

## CONCLUSION

The method proposed is satisfactory for routine work. Aluminium and titanium interfere, probably by forming the corresponding potassium–metal fluorides. Various efforts to keep these metals in solution have not yet succeeded. If these components, however, occur in relatively small concentrations as in our material, they cause no major errors. Calcium, on the other hand, often occurs in large quantities and interferes in the presence of trivalent iron. When the iron is reduced quantitatively to the divalent state, this difficulty is removed, and silica can be determined even in iron ore containing large quantities of calcium.

## ACKNOWLEDGEMENT

We wish to thank Dr. Y. SUNDSTRÖM for valuable criticism and helpful suggestions in the preparation of this paper.

## SUMMARY

A rapid and reliable routine method for determination of silica in iron ore has been developed and tested. The silica is converted to potassium fluosilicate by digestion with hydrofluoric acid, hydrochloric acid and potassium chloride and determined volumetrically.

## RÉSUMÉ

Une méthode de dosage rapide est proposée pour le dosage de la silice dans des minerais de fer. La silice est convertie en fluosilicate de potassium et dosée volumétriquement par l'hydroxyde de sodium.

## ZUSAMMENFASSUNG

Beschreibung einer Schnellmethode zur Bestimmung von Kieselsäure in Eisenerzen. Die Kieselsäure wird in Kaliumfluorosilikat übergeführt und mit Natronlauge titriert.

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# THE SEPARATION AND PHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM

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(Received January 2nd, 1961)

Methyl isobutyl ketone has been used widely in analytical chemistry for the extraction of chromium[1–4]. There have been no quantitative studies reported of the extraction of hexavalent chromium in the presence of pentavalent vanadium, and it was the purpose of the present investigation to develop a rapid method for the separation and determination of chromium and vanadium.

## APPARATUS AND REAGENTS

A Beckman Model DU spectrophotometer was used for all optical density measurements. It was equipped with 1-cm absorption cells. Extractions were made in 50-ml conical separatory funnels. The methyl isobutyl ketone (4-methyl-pentanone-2) was purchased from Coleman, Matheson and Bell, and from Eastman. It was distilled, and the fraction boiling between 114° and 116° was used for the extractions.

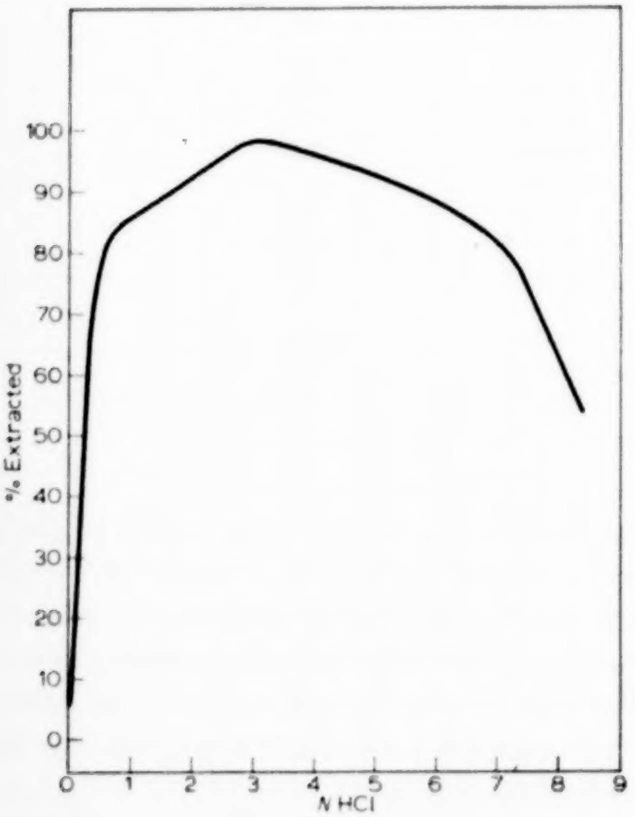

Fig. 1. The extraction of hexavalent chromium as a function of the aqueous hydrochloric acid concentration.

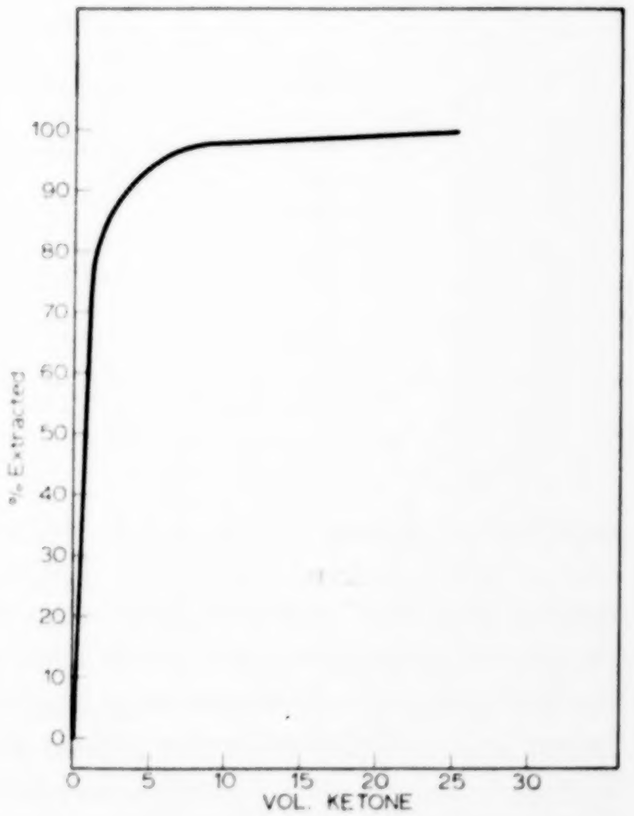

Fig. 2. The extraction of hexavalent chromium as a function of the volume of ketone.

## EXPERIMENTAL

### *Extraction studies*

Extraction studies were made on solutions of different acidities containing from 1–5 mg of hexavalent chromium using different amounts of solvent. 5-ml aliquots of potassium dichromate solutions of known chromium content were pipetted into separatory funnels, and increments of standard hydrochloric acid were added so that the acidities differed by 0.3 *N*. The solutions were diluted to a volume of 10 ml with water. The acid solutions were treated with a measured volume of methyl isobutyl ketone and shaken for 30 sec. The aqueous phase was separated and analyzed for chromium by a method suggested by WAGNER, HULL AND MARKLE[5]. The chromium was stripped from the ketone phase by washing with five 10-ml portions of water, and the washings were analyzed for chromium.

TABLE I

EXTRACTION OF HEXAVALENT CHROMIUM FROM 3 *N* HYDROCHLORIC ACID USING 25 ml OF METHYL ISOBUTYL KETONE

| *Chromium taken* mg | *Chromium found in ketone phase* mg | *Chromium found in aqueous phase* mg | *Amount extracted* % |
|---|---|---|---|
| 5.414 | 5.401 | 0.010 | 99.8 |
| | 5.376 | 0.033 | 99.3 |
| 4.873 | 4.872 | 0.006 | 100 |
| | 4.868 | 0.002 | 99.8 |
| 4.331 | 4.296 | 0.014 | 99.2 |
| | 4.329 | 0.010 | 100 |
| 3.790 | 3.789 | 0.000 | 100 |
| | 3.769 | 0.011 | 99.4 |
| 3.249 | 3.239 | 0.010 | 99.7 |
| | 3.248 | 0.003 | 100 |
| 2.707 | 2.686 | 0.012 | 99.2 |
| | 2.691 | 0.009 | 99.4 |
| | 2.689 | 0.013 | 99.4 |
| 2.166 | 2.152 | 0.013 | 99.4 |
| | 2.165 | 0.003 | 100 |
| | 2.158 | 0.010 | 99.6 |
| 1.624 | 1.614 | 0.010 | 99.4 |
| | 1.615 | 0.010 | 99.4 |
| | 1.620 | 0.005 | 99.8 |
| 1.083 | 1.078 | 0.004 | 99.5 |
| | 1.079 | 0.003 | 99.6 |
| | 1.074 | 0.006 | 99.4 |

The results of this study, as shown in Figs. 1 and 2 and in Table I, indicate that the hexavalent chromium was quantitatively extracted when the aqueous phase was 3 *N* in hydrochloric acid, and the volume of ketone was 25 ml.

The distribution of pentavalent vanadium was studied by extracting 3 *N* hydrochloric acid solutions of ammonium vanadate containing from 5–25 mg of vanadium with 25 ml of methyl isobutyl ketone and determining the vanadium content of the aqueous phase. The results of this study, as listed in Table II, indicate that less than 1.5% of the vanadium was extracted under these conditions.

TABLE II

EXTRACTION OF PENTAVALENT VANADIUM FROM 3 *N* HYDROCHLORIC ACID USING 25 ml OF METHYL ISOBUTYL KETONE

| *Vanadium taken* mg | *Vanadium found in ketone phase* mg (calc.) | *Vanadium found in aqueous phase* mg | *Amount extracted* % |
|---|---|---|---|
| 24.975 | 0.162 | 24.813 | 0.65 |
| | 0.264 | 24.711 | 1.06 |
| 19.820 | 0.102 | 19.718 | 0.52 |
| | 0.144 | 19.676 | 0.73 |
| 15.336 | 0.091 | 15.245 | 0.59 |
| | 0.082 | 15.254 | 0.54 |
| 10.244 | 0.081 | 10.163 | 0.78 |
| | 0.090 | 10.154 | 0.88 |
| 8.713 | 0.077 | 8.636 | 0.88 |
| | 0.072 | 8.641 | 0.82 |
| 6.970 | 0.064 | 6.906 | 0.92 |
| | 0.070 | 6.900 | 1.00 |
| 5.244 | 0.058 | 5.186 | 1.10 |
| | 0.051 | 5.193 | 0.97 |
| 5.112 | 0.047 | 5.065 | 0.92 |
| | 0.051 | 5.061 | 0.99 |
| 3.496 | 0.041 | 3.455 | 1.17 |
| | 0.036 | 3.460 | 1.03 |
| 1.748 | 0.021 | 1.727 | 1.20 |
| | 0.024 | 1.724 | 1.37 |

### *Preparation of calibration curves*

The absorption spectrum of hexavalent chromium extracted into methyl isobutyl ketone was studied in the 300- to 500-m$\mu$ range (Fig. 3). An absorption maximum was found at 444 m$\mu$. A plot of optical density against concentration at this wavelength gave a straight line with a slope of 3.41, and an extinction coefficient of 3.42 ± 0.07 ml/cm/mg was calculated from the data in Table III.

The work of SANTINI, HAZEL AND McNABB[6] showed that the vanadyl ion is suitable for photometric analysis. Therefore, the absorption spectrum of ammonium vanadate saturated with methyl isobutyl ketone in 3 *N* hydrochloric acid and reduced with

## TABLE III

OPTICAL DENSITIES OF VARIOUS AMOUNTS OF HEXAVALENT CHROMIUM IN 25 ml OF METHYL ISOBUTYL KETONE AT 444 mμ

| *Conc. Cr taken mg/ml* | *Optical density* | *ε = optical density/conc. ml/mg* |
|---|---|---|
| 0.2166 | 0.732 | 3.38 |
| 0.1949 | 0.655 | 3.35 |
| 0.1732 | 0.594 | 3.43 |
| 0.1516 | 0.512 | 3.38 |
| 0.1299 | 0.444 | 3.42 |
| 0.1083 | 0.368 | 3.39 |
| 0.0866 | 0.300 | 3.46 |
| 0.0649 | 0.220 | 3.39 |
| 0.0433 | 0.156 | 3.60 |

## TABLE IV

OPTICAL DENSITIES OF VARIOUS AMOUNTS OF TETRAVALENT VANADIUM IN 3 *N* HYDROCHLORIC ACID SATURATED WITH METHYL ISOBUTYL KETONE AT 760 mμ

| *Conc. V taken mg/ml* | *Optical density* | *ε = optical density/conc. ml/mg* |
|---|---|---|
| 2.891 | 0.943 | 0.325 |
| 2.478 | 0.800 | 0.325 |
| 2.065 | 0.665 | 0.322 |
| 1.652 | 0.532 | 0.322 |
| 1.239 | 0.397 | 0.320 |
| 0.826 | 0.270 | 0.326 |
| 0.413 | 0.135 | 0.326 |

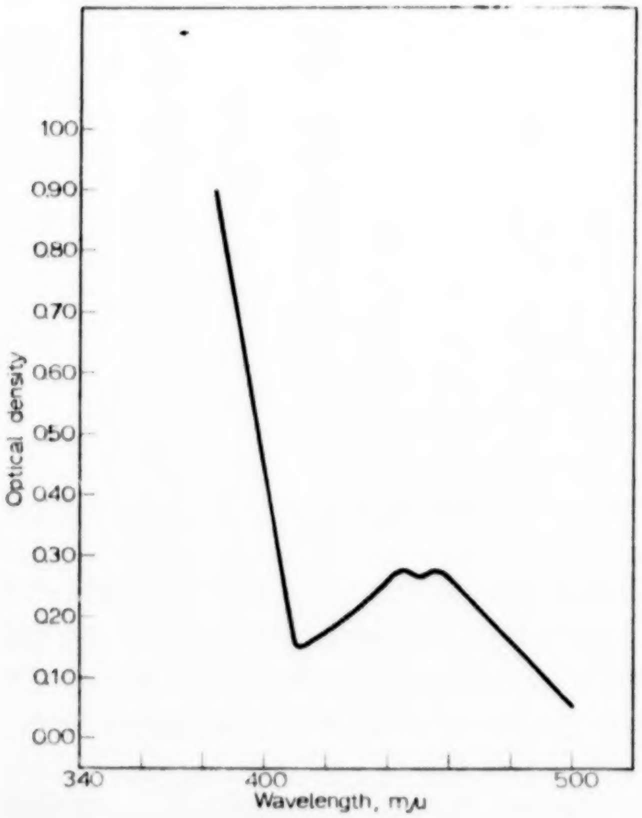

Fig. 3. The absorption spectrum of hexavalent chromium in the ketone phase.

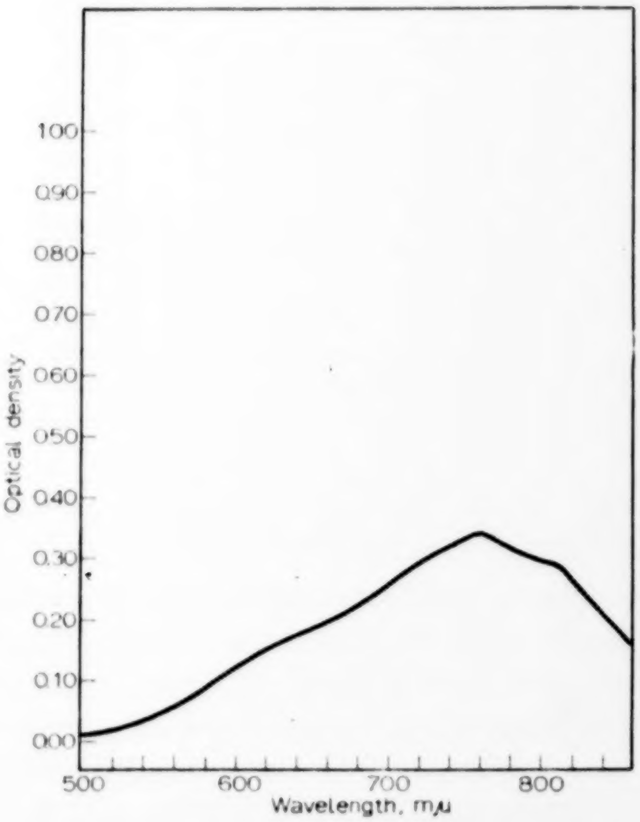

Fig. 4. The absorption spectrum of reduced vanadium in the aqueous phase.

sodium metabisulfite to vanadyl sulfate was studied in the 500- to 900-m$\mu$ range (Fig. 4). An absorption maximum was found to occur at 760 m$\mu$. A plot of optical density against concentration gave a straight line with a slope of 0.324, and an extinction coefficient of 0.322 ml/cm/mg was calculated from the data in Table IV.

*Color stability studies*

In order to determine if any reduction occurred, as reported by HEILBORN[7], a solution of potassium dichromate was acidified and extracted. Optical density measurements of the organic phase were made every 10 min for 3 h. These data, as shown in Fig. 5, revealed that there was no change in optical density during the first 30 min. However, after 30 min, the optical density was found to decrease. It is apparent that these measurements must be made immediately after extraction.

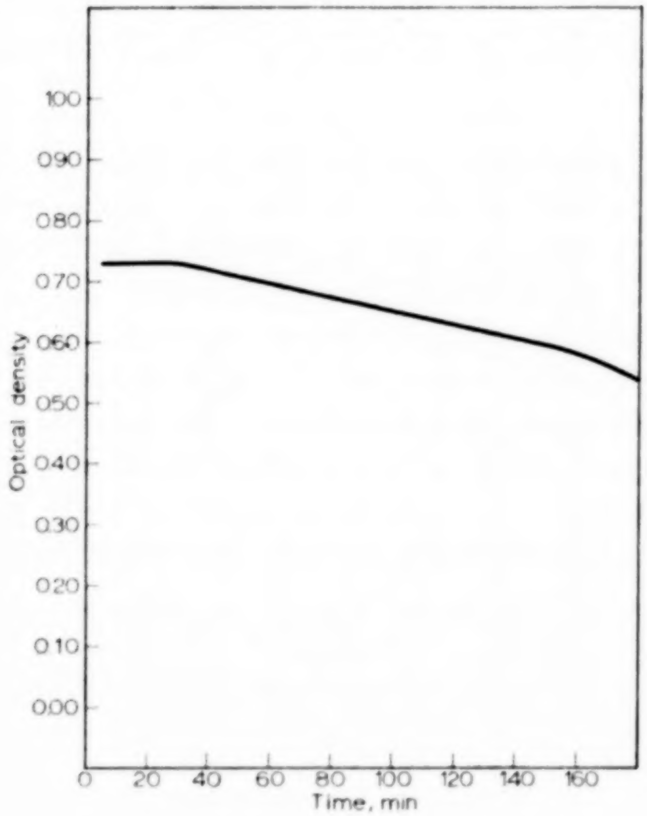

Fig. 5. Optical density of hexavalent chromium in the ketone phase as a function of time.

A similar study was made of the reduced vanadium in the aqueous phase. It was found that the color was stable for 20 h.

*Determination of chromium and vanadium in mixtures*

Aliquots of standard solutions of potassium dichromate and ammonium vanadate were mixed, treated with 5 ml of 6 N hydrochloric acid, and brought to a volume of 10 ml with water. The acidic solutions were shaken for 30 sec with 25 ml of methyl isobutyl ketone. The optical density of the ketone phase was measured at 444 m$\mu$, and the chromium content was calculated from this measurement.

The aqueous phase was treated with 0.5 g of sodium metabisulfite, and the solution was boiled for 10 min. This solution was cooled, transferred to a 10-ml volumetric flask, and diluted to the mark with water. From the optical density measurement at 760 m$\mu$, the vanadium content was calculated. The results are given in Table V. The error noted in the table is of the order inherent in colorimetric methods.

TABLE V

RESULTS OF CHROMIUM AND VANADIUM DETERMINATIONS IN MIXTURES

| *Cr taken mg/ml* | *V taken mg/ml* | *Cr found mg/ml* | *V found mg/ml* |
|---|---|---|---|
| 0.49 | 0.00 | 0.47 | 0.00 |
| 0.49 | 1.02 | 0.47 | 1.04 |
| 0.49 | 2.05 | 0.47 | 2.10 |
| 0.24 | 2.05 | 0.25 | 2.07 |
| 0.00 | 2.05 | 0.00 | 2.06 |

### *Steel analysis*

A 1-g sample of steel shavings (steel containing approximately 2.5% Cr and 1% V) was weighed out and transferred to a 250-ml beaker. The sample was treated with 20 ml of 3 *M* sulfuric acid and 4 ml of 6 *M* phosphoric acid. The mixture was heated until reaction ceased. 2 ml of concentrated nitric acid was added, and the solution was boiled until brown fumes were no longer expelled. The solution was diluted to approximately 50 ml, treated with 1 ml of 0.1 *M* silver nitrate and 5 ml of 20% potassium persulfate solution, and boiled until the color of permanganate was observed. 5 ml of 6 *M* hydrochloric acid was added to destroy this color. The solution was boiled until its volume was reduced to approximately 30 ml, neutralized with approximately 30 ml of 6 *N* sodium hydroxide, and filtered into a 100-ml volumetric flask. The precipitate was washed with two 10-ml portions of water. The washings were added to the flask, and the contents were diluted to the mark with water. A 5-ml aliquot of this solution was transferred to a separatory funnel and treated as described above. The results of two steel analyses are reported in Table VI. In the case of the second sample, better results would have been obtained with a 2-g sample.

TABLE VI

RESULTS OF CHROMIUM AND VANADIUM DETERMINATIONS IN STEEL

| *Cr reported %* | *V reported %* | *Cr found %* | *V found %* |
|---|---|---|---|
| 3.52 | 0.97 | 3.55 | 0.96 |
| | | 3.54 | 0.97 |
| | | 3.54 | 0.96 |
| 0.95 | 0.18 | 0.94 | 0.12 |
| | | 0.94 | 0.13 |
| | | 0.94 | 0.13 |

## SUMMARY

A study was made on the extraction of hexavalent chromium from hydrochloric acid solutions with methyl isobutyl ketone. Quantitative extraction was accomplished from 3 *N* hydrochloric acid with 25 ml of solvent. Under these conditions, it was found that chromium could be extracted from vanadium. A procedure was developed for the colorimetric determination of chromium in the ketone phase and of vanadium in the aqueous phase. The analytical procedure was used to analyze standard steel samples for chromium and vanadium, and the results obtained by this method were found to agree with the accepted values.

## RÉSUMÉ

Une étude a été effectuée sur l'extraction du chrome(VI), en solution chlorhydrique, au moyen de méthylisobutylcétone. Il est possible de séparer ainsi le chrome du vanadium. Une méthode colorimétrique est décrite pour le dosage de ces deux éléments, en particulier dans les aciers.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung von Chrom(VI) und Vanadium durch Extraktion mit Methylisobutylketon mit anschliessender colorimetrischer Bestimmung der beiden Elemente.

## REFERENCES

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# A NEW SPECIFIC TEST FOR ALUMINIUM

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(Received January 27th, 1961)

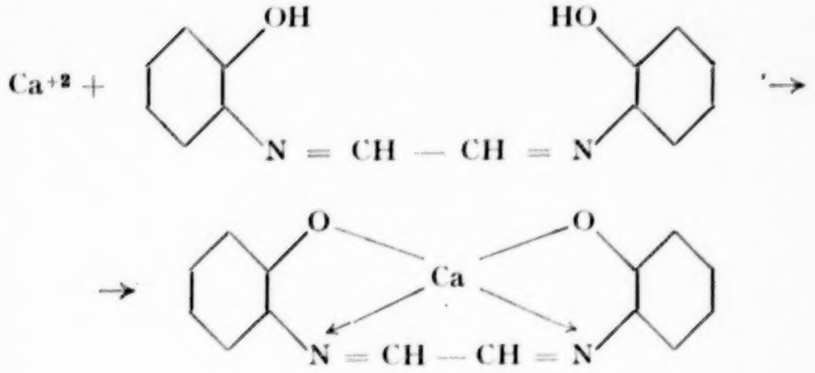
It has been shown by FEIGL[1] that "demasking" reactions can be successfully used for the sensitive detection of materials, by causing the formation of new, more stable complexes through the liberation of previously "masked" ionic species. The demasking reactions of ferrocyanide[2], yellow palladium dimethylglyoxime complex[3] and zirconium alizarinate[4] have been used for the detection of mercury(II), cyanide and fluoride respectively.

The present paper provides a new example of how differences in the stability of colourless inorganic complexes may be indicated by colour tests and utilized for analytical purposes.

From insoluble calcium fluoride, calcium ions are liberated by the addition of aluminium ions, owing to the formation of the highly stable $[AlF_6]^{-3}$ complex. The subsequent detection of calcium ions by the recently reported specific method of

**Goldstein and Stark-Mayer**[5] makes possible a new specific test for aluminium, *i.e.*:

$$3\ CaF_2 + Al^{+3} \rightarrow [AlF_6]^{-3} + 3\ Ca^{+2} \qquad (1)$$



(2)

As the displacement of calcium (eqn. 1) was found to be restricted to aluminium among a series of ions tested under certain conditions, and as the formation of the inner complex of calcium with glyoxal bis(2-hydroxyanil) (eqn. 2) has been shown to form a basis for a strictly specific test for calcium, the above process is recommended as a reliable and specific method for the detection of aluminium.

## EXPERIMENTAL

### *Materials*

Glyoxal bis(2-hydroxyanil) was prepared by **Bayer**'s method[6]: 4.4 g of *o*-aminophenol were dissolved in 1 l of water at 80° and 3.0 g of 40% aqueous solution of glyoxal was added. The mixture was kept at 80° for 30 min and then for 12 h in an ice box. The precipitate was filtered, washed with water and recrystallized from methanol. A 1% alcoholic solution of the reagent was used. All the other materials used were of analytical grade.

### *General procedure*

A few mg of pure calcium fluoride were placed in a micro test tube, and a drop of the neutral or slightly acidic test solution was added followed by a few drops of the reagent solution and one drop of 10% sodium hydroxide and 10% sodium carbonate solution. The precipitate formed was extracted with a few drops of chloroform. The presence of aluminium was indicated by the appearance of a red colour in the organic layer. (A blank test should be carried out for comparison).

Identification limit: 0.5 μg Al.
Dilution limit: 1 : 100,000.

### *Interferences*

The presence of a relatively large amount of any of the following ions does not interfere with the test: Na, K, Mg, Sr, Ba, ZrO, Cr, Mn, Fe, Co, Ni, Mo, W, Re, Ru, Rh, Pt, Cu, Ag, Au, Zn, Hg, B, Ga, Tl, Ge, Sn, Pb, As, Sb, Bi, U, Ce.

In view of the similar displacing effects on calcium fluoride of both beryllium and aluminium, the test should be carried out in tartaric acid solution, which forms a stable complex with beryllium.

It has been found by previous workers that cadmium also reacts with the reagent under similar conditions to calcium, and the blue product obtained is extractable with chloroform. This interference may, however, be eliminated[5] if a 10% sodium cyanide solution is introduced in addition to the 10% sodium hydroxide solution as described in the general procedure.

Calcium ions obviously interfere with the test, but this difficulty may be overcome by the precipitation of calcium as the oxalate, followed by filtration.

It should be pointed out that the test solution must be neutral or slightly acidic. If the pH of the test solution is less than 2, calcium ions are liberated from the fluoride. On the other hand, if the pH of the solution exceeds 8, the demasking of calcium by aluminium does not occur.

### SUMMARY

A new specific spot test for aluminium is described. The test is based on the demasking action of aluminium ion on calcium fluoride, and subsequent detection of the liberated calcium by glyoxal bis-(2-hydroxyanil).

### RÉSUMÉ

Une nouvelle réaction à la touche, spécifique, est décrite pour l'identification de l'aluminium. On utilise comme réactif le fluorure de calcium; l'aluminium se complexant avec le fluorure, le calcium est libéré et peut réagir avec le bis-(hydroxy-2-anil)-glyoxal.

### ZUSAMMENFASSUNG

Beschreibung einer neuen, spezifischen Nachweisreaktion (Tüpfelprobe) für Aluminium durch Komplexbildung mit Calziumfluorid und Nachweis des dabei in Freiheit gesetzten Calziums mit Bis-(2-hydroxyanil)-glyoxal.

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[4] I. H. DE BOER, *Chem. Weekblad*, 21 (1924) 404.
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[6] E. BAYER, *Chem. Ber.*, 90 (1957) 2325.

*Anal. Chim. Acta*, 25 (1961) 199–201

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# Short Communications

## Applications de la chélatométrie
## XIV. Dosage volumétrique des *vic*-dicétones

Nous avons montré, en collaboration avec MERLIN[1] que le diacétyle, premier terme des *vic*-dicétones, pouvait être dosé par chélatométrie: aprés réaction avec le chlorhydrate d'hydroxylamine en présence d'acétate de sodium et d'acétate de nickel, le diacétyle est complètement précipité sous forme de diméthylglyoximate de nickel et il suffit de titrer le nickel en excès après filtration; on emploi pour cela l'acide éthylène-diaminotétracétique en milieu ammoniacal et la murexide comme indicateur.

Utilisant le même mode de précipitation des dioximates de nickel nous avons

ensuite, en collaboration avec VIEILLET[2], montré la possibilité de doser, toujours par chélatométrie, quelques *vic*-dioximes d'emploi fréquent en analyse minérale.

Dans le premier travail[1] nous avions émis la supposition que la méthode décrite pourrait être employée pour les homologues supérieurs du diacétyle; la présente communication a pour but de rapporter les essais que nous avons effectués sur quelques uns de ces produits. La seule modification apportée dans le processus opératoire consiste dans un retard que nous avons observé pour l'introduction de l'acétate de nickel; en même temps que l'échantillon pesé et le chlorhydrate d'hydroxylamine *N*, nous avons introduit 10 ml d'une solution aqueuse d'acétate de sodium $CH_3COONa \cdot 3\,H_2O$ à 410 g/l; 25 ml d'une solution aqueuse d'acétate de nickel $(CH_3COO)_2Ni \cdot 4\,H_2O$ à 50 g/l ont été introduits seulement après trois heures d'ébullition, soit donc une heure avant la fin du traitement. Cette modification n'a d'autre but que de faciliter l'oximation en travaillant dans un milieu plus riche en alcool et donc meilleur solvant.

TABLEAU I

| *Produit essayé* | *Poids mg* | *Titre trouvé* | *Déviation %* |
|---|---|---|---|
| 2,3-pentane dione | 513 | 98.8 | — 1.2 |
| | 521 | 99.2 | — 0.8 |
| | 527 | 98.7 | — 1.3 |
| | 509 | 99.0 | — 1.0 |
| 2,3-pentane dione + diéthylcétone 75:25 | 681 | 74.3 | — 0.9 |
| | 672 | 74.3 | — 0.9 |
| | 609 | 74.2 | — 1.1 |
| 2,3-pentane dione + diéthylcétone 50:50 | 802 | 49.3 | — 1.4 |
| | 823 | 49.5 | — 1.0 |
| | 837 | 49.3 | — 1.4 |
| 1-phényl 1,2-propane dione | 708 | 98.2 | — 1.8 |
| | 717 | 98.5 | — 1.5 |
| | 723 | 98.3 | — 1.7 |
| 1,2-cyclohexane dione | 502 | 98.8 | — 1.2 |
| | 523 | 98.9 | — 1.1 |
| | 549 | 99.1 | — 0.9 |
| 1-méthyl 2,3-cyclohexane dione | 608 | 98.4 | — 1.6 |
| | 581 | 98.2 | — 1.8 |
| | 597 | 98.5 | — 1.5 |

Le Tableau I résume les résultats que nous avons obtenus.

*Seraincourt, Seine et Oise (France)* C. HENNART

1 C. HENNART ET E. MERLIN, *Chim. anal.*, 41 (1959) 287.
2 C. HENNART ET F. VIEILLET, *Anal. Chim. Acta*, 25 (1961) 150.

Reçu le 24 janvier, 1961

# Potentiometric titration of thallium(III) with chromium(II) solution

Recently certain methods for the determination of thallium(III) based on reductimetric titration with titanium(III) and ascorbic acid have been studied in these laboratories; although the reactions are quantitative, they are rather sluggish in dilute solutions near the end-point. Titration with chromium(II) solution was therefore examined.

Chromium(II) solutions are the strongest reductimetric titrants used, as indicated by the standard redox potential[1] —0.41 *vs.* the normal hydrogen potential; they therefore have certain advantages over other reagents such as titanium(III)[2]. Although the reduction is smooth even at room temperature with chromium(II) solutions, great care must be taken to protect the titrant from atmospheric oxidation and to prepare it from pure compounds[3]. Difficulties involved with visual indicators for the end-point were eliminated by using a potentiometric titration. Irreversible indicators such as methyl orange were examined but it was necessary to apply an indicator correction. The potentiometric method was found to be generally more satisfactory.

An approximately (0.05 $N$) chromium(II) solution was prepared by the reduction of A.R. potassium dichromate by hydrogen peroxide and amalgamated zinc[4], the overall acid concentration being about 2–3 $N$, and the solution was stored in an automatic burette. A standard (0.05 $M$) thallium(III) solution was prepared by dissolving the required amount of thallic oxide (Spec-pure) in concentrated sulphuric acid and then diluting to a definite volume. The chromium(II) solution was standardised against iron(III) solution while the strength of the thallium(III) solution was checked iodometrically.

The titrations were performed in a three-necked flask holding the carbon dioxide tube, platinum electrode and an agar-agar bridge connected to an external calomel electrode; a Doran pH meter (Universal Model No. 4981) was used for $E$ measurement.

For a determination, an aliquot of thallium(III) solution was treated with bromine[5] to ensure that all the thallium was present in the trivalent state. The titrations were performed at an acid concentration of 2–3 $N$ in an atmosphere of oxygen-free carbon dioxide, the end-point being indicated by a fall in $E$ of the order of 110–130 mV. The temperature of the titration was 30–35°. The results of determinations of thallium(III) at varying concentrations are shown in Table I.

TABLE I

DETERMINATION OF THALLIUM(III)

| *Thallium(III) taken in 20 ml soln. (mg)* | *Chromium(II) added (ml)* | *Thallium(III) found (mg)* | *% deviation* |
|---|---|---|---|
| 100.00 | 19.63 | 100.11 | 0.11 |
| 110.60 | 21.70 | 110.67 | 0.06 |
| 115.60 | 22.70 | 115.77 | 0.14 |
| 125.00 | 24.70 | 125.97 | 0.77 |

When methyl orange (2 drops of a 1% solution) was used as indicator, the same preoxidation, acidity and inert atmosphere were used as for the potentiometric titration. The end-point was indicated by irreversible bleaching of the pink colour of the indicator. The results obtained were slightly higher than those obtained by the potentiometric method, unless an indicator blank was determined and deducted.

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RITA MAJUMDAR
M. L. BHATNAGAR

[1] G. GRAUBE AND G. BRINTZINGER, *Z. Elektrochem.*, 33 (1927) 112.
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Received January 25th, 1961

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## Announcement

### INTERNATIONAL CONFERENCE ON SPECTROSCOPY
### CONFÉRENCE INTERNATIONALE DE SPECTROSCOPIE
### INTERNATIONALE KONFERENZ FÜR SPEKTROSKOPIE

June 18 to June 22, 1962

*University of Maryland, College Park (Md., U.S.A.)*

Organized by the
*Society for Applied Spectroscopy*

The purpose of this conference is to promote the interchange of information across disciplinary and geographical boundaries.

The technical program will consist of a number of lectures by internationally noted spectroscopists as well as sessions for submitted papers. Topics covered by the program are: emission, X-ray, infrared, NMR, EPR, microwave, astrophysical, and mass spectroscopy. In addition, there will be a session on education in spectroscopy. The latest spectrographic equipment will be exhibited by the manufacturers.

Those desiring to present papers should submit titles and abstracts of 300 words or less to the conference chairman before December 1, 1961. All individuals interested in further details should send their name and address to:

Mr. BOURBON F. SCRIBNER, Conference Chairman, International Spectroscopy Conference, National Bureau of Standards, Washington 25, D.C. (U.S.A.)

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
## Vol. 25, No. 3, September 1961

### PROF. DR. ING. FRITZ FEIGL

*(Biography)*

*Anal. Chim. Acta*, 25 (1961) 205–207

### APPLICATION OF ORGANOSELENIUM COMPOUNDS IN ANALYTICAL CHEMISTRY

#### III. MONOCHLOROSELENODIPHENYLAMINE AS NEW REAGENT FOR PALLADIUM

*(in French)*

Studies on the application of organoselenium compounds have been continued. Monochloroselenodiphenylamine is suggested as a new sensitive and selective reagent for palladium; the complex obtained has been analysed.

F. Pino Pérez, F. Burriel-Martí and F. J. Mateo, *Anal. Chim. Acta*, 25 (1961) 207–211

### THE EFFECT OF ORGANIC SUBSTITUENTS AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS ON THEIR EXTRACTION ABILITIES FOR URANIUM

With 12 phosphates, 1 phosphonate, 1 phosphinate and 1 phosphine oxide, the pattern of uranium extraction from nitric acid media was investigated. The extraction was affected by the nature of the organic substituents attached to the phosphoryl group as well as by the solvent structure. Phosphates with aryl groups were not satisfactory extractants. The extraction ability increased as the alkyl group was made larger; phosphates with branching alkyl groups were better than phosphates with normal alkyl groups. Removal of the alkoxyl oxygen enhanced the extracting abilities. The relative order of the extracting abilities were: tri-*n*-butyl phosphine oxide and tri-*n*-butyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups.

S. Nomura and R. Hara, *Anal. Chim. Acta*, 25 (1961) 212–218

### HYDRAZINE AS A GENERAL TITRIMETRIC REAGENT IN IODIMETRY

#### PART II

The general method involving hydrazine as a substitute for thiosulphate in iodimetry has been extended for the determination of organic compounds containing carbonyl, phenolic and sulphydryl groups and for some sulphur- and nitrogen-containing compounds and aldoses.

K. S. Panwar, S. P. Rao and J. N. Gaur, *Anal. Chim. Acta*, 25 (1961) 218–221

## SEPARATION OF URANIUM BY ANION EXCHANGE

A method for the separation of uranium(VI) from numerous elements by means of anion exchange is described; the negatively charged chloride complex of uranium is adsorbed on the strongly basic anion exchanger Dowex 1X8 (chloride form) from a solution containing 80% methanol and 20% 6 *N* hydrochloric acid. The uranium was determined by a polarographic method based on the catalytic nitrate wave of uranium.

F. TERA AND J. KORKISCH, *Anal. Chim. Acta*, 25 (1961) 222–225

## ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co

### III. PAPER CHROMATOGRAPHY

Paper chromatographic separations are described by which the minor constituents of biological ashes are separated either into: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; or into: Cu, Mn, Co – Pb – Fe – Mo – Zn.

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 25 (1961) 226–232

## ABSORPTIOMETRIC DETERMINATION OF SULFATE IN WATERS

An absorptiometric method is proposed for sulfate determination, based on the colour produced by heating sulfuric acid with saccharose at 85° for 60 min. The method was applied to the determination of sulfate in treated waters; chloride was removed by precipitation with silver acetate, and sulfate was converted to sulfuric acid with a cation exchange resin column.

O. A. OHLWEILER AND J. O. MEDITSCH, *Anal. Chim. Acta*, 25 (1961) 233–237

## THE DETERMINATION OF MAGNESIUM WITH TITAN YELLOW

A study was made of the different factors which influence the colorimetric determination of magnesium with titan yellow, namely, the titan yellow product, the protective colloid, the colour stabilizer and the sodium hydroxide. Interfering elements were separated by precipitation with sodium tungstate. Several improvements were introduced.

J. CH. VAN WESEMAEL, *Anal. Chim. Acta*, 25 (1961) 238–247

## THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM WITH *ortho*-DIANISIDINE

A spectrophotometric method for the determination of chromium(VI) and vanadium(V), when present singly or together, in presence or absence of iron(III), has been developed, by exploiting the color changes which result from the oxidation in strongly acid medium of *ortho*-dianisidine by these metal ions.

M. ARIEL AND J. MANKA, *Anal. Chim. Acta*, 25 (1961) 248–256

## A STUDY OF SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

Six derivatives of 1,10-phenanthroline have been prepared in which the substituents are present in the 'pyridine' ring. The relative stabilities of the complexes formed by these compounds with iron(II) have been determined spectrophotometrically, and have been related to the basicity of the ligands. It was found that stability was related to this basicity but other effects such as the mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance were also significant.

C. J. Hawkins, H. Duewell and W. F. Pickering, *Anal. Chim. Acta*, 25 (1961) 257–261

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## THE EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH 1,1'-DIANTHRIMIDE

The effects of about 40 inorganic ions and reducing and oxidizing agents on the determination of boron with 1,1'-dianthrimide were studied spectrophotometrically. The separate foreign ions were added both to solutions containing boron and 1,1'-dianthrimide and to solutions containing only 1,1'-dianthrimide. From the two series of extinction measurements conclusions were drawn as to the type of interference present. With the use of hydrazine sulphate as reducing agent, the only ions interfering were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. A new method of indicating spectrophotometric interference was introduced.

F. J. Langmyhr and O. B. Skaar, *Anal. Chim. Acta*, 25 (1961) 262–270

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## SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN GEOLOGICAL MATERIALS USING SPECTRAL LINE WIDTH

Line width, used as a measure of potassium concentration, is superior to spectral line density (or percent transmission) in a general DC arc spectrographic method for the determination of K in geological materials.

J. N. Weber, *Anal. Chim. Acta*, 25 (1961) 270–273

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## APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

### I. LEAD-BASE ALLOYS

The application of controlled-potential electrolysis to the determination of copper, lead and tin, after titration of antimony, is discussed for the analyses of lead-base and tin-base alloys.

B. Alfonsi, *Anal. Chim. Acta*, 25 (1961) 274–280

## POLAROGRAPHY OF SOME PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

The polarographic characteristics of 2-, 3-, and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides are reported. Well-defined, diffusion controlled, cathodic waves were observed, with the exception of pyridine-3-aldoxime, over the pH range 0–12 for the overall irreversible reduction of the oxime group to a primary amine, a process which involves the uptake of four electrons. The 1-methylpyridinium alsoximes were more easily reduced than were the corresponding pyridine aldoximes, particularly at high pH values where the pyridine nitrogen was unprotonated. Within each series the ease of reduction was as follows: 4->2->3-substituents. At high pH values a second cathodic wave was also observed in the case of the 1-methylpyridinium aldoximes which corresponded to reduction of the methylpyridinium nucleus. Alternating current polarographic studies indicated that the electrode process involved some reversible electrochemical steps. In addition, maximum suppressors were observed to shift half-wave potentials to more negative values without altering diffusion currents.

N. G. Lordi and E. M. Cohen, *Anal. Chim. Acta*, 25 (1961) 281–288

## DISSOCIATION CONSTANTS OF CHROMAZUROL S

*(Short communication; in German)*

M. Malát, *Anal. Chim. Acta*, 25 (1961) 289–291

## SEPARATION OF ANTIMONY(III) BY ION-EXCHANGE

*(Short communication)*

S. S. M. A. Khorasani and M. H. Khundkar, *Anal. Chim. Acta*, 25 (1961) 292–293

## DETERMINATION OF TRACES OF CYANIDE

*(Short communication)*

G. V. L. N. Murty and T. S. Viswanathan, *Anal. Chim. Acta*, 25 (1961) 293–295

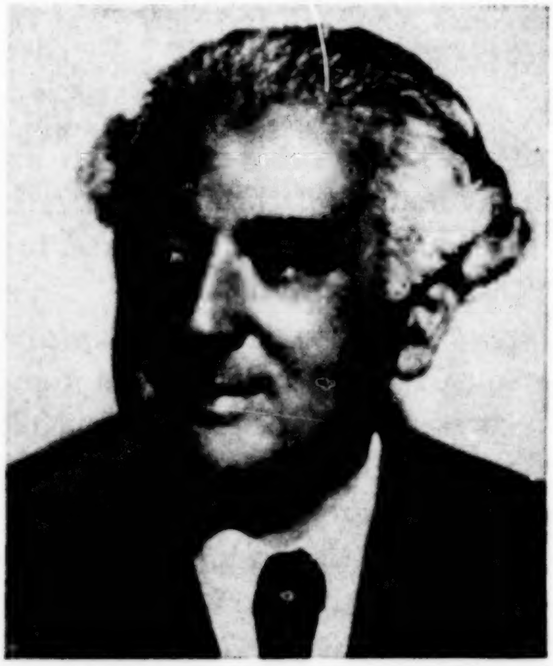
## A SENSITIVE, RAPID DETERMINATION OF INORGANIC PHOSPHATE IN PRESENCE OF LABILE PHOSPHATE ESTERS

*(Short communication)*

H. L. Golterman and I. M. Wurtz, *Anal. Chim. Acta*, 25 (1961) 295–297

# PROF. Dr. ING. FRITZ FEIGL

When Prof. Dr. Ing. Fritz Feigl celebrated his 70th birthday on May 15, 1961, in his native city of Vienna, he stood in undiminished vitality at the pinnacle of success. Both fundamental and applied science owe him a great debt for the contributions which he has made and the stimulus he has provided in all branches of analytical chemistry, and we take this opportunity to wish him many more years of health and fruitful investigation.



Fritz Feigl

Feigl was born 1891 in Vienna and is today Director of one of the most important Departments of the Ministerio da Agricultura in Brazil. He began his studies under Vortmann and Strebinger at the Technische Hochschule in Vienna and made an immediate impression with an independent study of the mixed sulfides produced by treatment with hydrogen sulfide. His first small publication appeared in 1914. His professors had no great opinion of the new ideas of their pupil, and some years passed before Strebinger, at least, recognized the genius which was to lead to the creation of spot analysis as an independent and creative branch of analytical chemistry.

A great break in FEIGL's scientific development was caused by the First World War throughout which he served, first as a soldier and then as an officer. He was awarded the Military Service Bronze and Silver Medals and the Military Service Cross and was wounded during the hostilities.

In 1919 he became an Assistant in the II. Chemical Laboratory of the University of Vienna, but this did not satisfy his enthusiasm for work, and he played a large part in the development of the Chemical Laboratory of the Ottakringer Volksheim, where he remained Director until 1938. The year 1921 saw the publication of *Die Verwendung von Tüpfelreaktionen in der qualitative Analyse* which is today considered the fountainhead of spot analysis. In 1923 followed the publication of *Tupfelanalyse und Farbreaktionen als mikrochemische Arbeitsmethoden*. In 1927, he was appointed Lecturer in the University of Vienna. As interest in the new method of analysis grew FEIGL was awarded the Haitinger Prize by the Austrian Academy of Sciences in 1929 for his contributions to qualitative analysis with inorganic and organic reagents. The latter class of reagent owes much of its present universal acceptance to FEIGL's impetus.

His first book, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* was published in 1931, an English edition published by Elsevier following shortly afterwards. This book has now gone through six revisions, with the latest edition appearing as two volumes: *Spot Tests in Inorganic Analysis* and *Spot Tests in Organic Analysis*. These books have been recognized for many years as classics of analytical chemistry.

In 1932, FEIGL became Director of the Qualitative Department of the Chemical Laboratory of the University of Vienna, and in 1935, he became Professor. In 1938, he was forced to flee from his homeland through Switzerland to Ghent, and then, as tide of the Second World War rose, to England and finally to Brazil, where he found eventually a permanent and congenial home.

In 1949 he published another classic book, *The Chemistry of Specific, Selective and Sensitive Reagents*, which constitutes a milestone in the development of modern analytical chemistry. At the present time, he has published approximately 400 papers dealing with reactions which can be applied analytically. The many analytical applications of catalyzed and induced reactions, fluorescence and solid body reactions are all fundamentally based on FEIGL's work. And still his fertile mind utilizes an unparalleled knowledge of chemical reactions to extend the limits of analytical chemistry in many branches.

During recent years, FEIGL has put out a series of papers in which he has clearly demonstrated that entirely new paths can be followed in qualitative organic analysis, through the intelligent use of syntheses and modes of reaction of the material whose detection is the goal. He has made brilliant use of pyrolytic procedures, including pyrohydrolysis and pyroammonolysis. These original studies open completely new perspectives in the development of qualitative organic analysis. During recent years, and particularly the last five years, FEIGL has discovered over 100 new tests for organic compounds and/or the functional groups they contain. He has succeeded in solving many analytical problems including some where physical methods fail.

His outstanding achievements have brought him many honors and distinctions including the Pregl Prize of the Austrian Academy of Sciences, the Emich Medal of the Austrian Society for Microchemistry, the Einstein Medal of the Brazilian Academy of Sciences, the Weizmann Prize for Exact Sciences of Israel and the Talanta Medal. He is a Doctor *honoris causa* of the Universities of Brazil and of Sao Paulo and of the Technische Hochschule of Vienna, a member of the Austrian and Brazilian Academies of Sciences, and an honorary member of chemical societies in Austria, Brazil, England, Switzerland and Japan. He has been Honorary Chairman of the Louisiana State University *Symposium on Modern Methods of Analytical Chemistry* and has been a featured speaker at a summer symposium on *Organic Reagents for Inorganic Analysis* sponsored by the Analytical Division of the American Chemical Society as well as at many other scientific meetings.

Rather than to dedicate a volume at the present time to this very highly distinguished member of their Editorial Board, the Editors of this Journal are assisting in the organization of the Symposium which is to be held next year in FEIGL's honor and which is announced below. The Proceedings of the Symposium will be published as a Supplement to this Journal.

### FEIGL ANNIVERSARY SYMPOSIUM, 1962

*Held in honor of Professor* FRITZ FEIGL *to Commemorate his 70th Birthday*

An International Symposium on Analytical Chemistry to honor Prof. FRITZ FEIGL, will be held in the University of Birmingham, England, on the 9–12th April, 1962. Further details will be announced shortly. The Secretary of the Symposium will be M. L. RICHARDSON, c/o John and E. Sturge Ltd., Lifford Chemical Works, Kings Norton, Birmingham 30, England.

P.W.W.
A.M.G.M.

*Anal. Chim. Acta*, 25 (1961) 205–207

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# APPLICATION DES COMPOSÉS ORGANOSÉLÉNIQUES À LA CHIMIE ANALYTIQUE

## III. LA MONOCHLOROSÉLÉNODIPHÉNYLAMINE, NOUVEAU RÉACTIF DU PALLADIUM

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(Reçu le 10 janvier 1961)

Nous poursuivons dans le présent travail, l'étude des composés organiques du sélénium, comme réactifs des métaux nobles[1,2], et nous proposons comme réactif du palladium la monochlorodiphénylamine.

En tachant de synthétiser la sélénodiphénylamine selon CORNELIUS[3] par la réaction entre la diphénylamine et différents chlorures de sélénium dans une solution benzénique, nous nous sommes trouvés au début avec certaines difficultés, dérivées du choix du chlorure de sélénium à employer.

Cependant, après de très profondes études sur ces réactions et suivant tout d'abord les principes donnés par SIMONS[4], YORST ET KURCHER[5], nous sommes arrivés par le procédé exposé ci-dessous à synthétiser pour la première fois, la *sélénodiphénylamine chlorée*, dont le résultat a été d'avoir eu un grand intérêt analytique comme on verra après, spécialement comme réactif du palladium*.

### SYNTHÈSE DE LA SÉLÉNODIPHÉNYLAMINE MONOCHLORÉE

Dans un matras d'une contenance environ de 2½ l, on y verse 2 l de benzène et 12 g de $SeCl_4$; le benzène prend une couleur jaune clair et dégage une grande quantité de vapeurs de HCl.

Une fois dissous le $SeCl_4$, on y ajoute, en le versant par la partie supérieure du réfrigérant, 10 g de diphénylamine dissous dans un petit volume de benzène. La solution devient d'une couleur rouge-foncé. On chauffe encore au reflux pendant 45–60 min. Lorsque le dégagement des vapeurs est fini, on distille le benzène jusqu'à un volume de 150 ml environ. Transvaser dans un Erlenmeyer à bouchon à l'émeri, et laisser reposer dans le frigidaire.

C'est très important que la distillation soit faite à une pression réduite et s'il est possible, sous une atmosphère inerte (nous avons distillé sous azote). La température de distillation doit être aussi basse que possible pour réduire la décomposition et éviter ainsi que le produit devienne résineux. Nous avons travaillé dans un vide qui nous permettait de distiller le benzène à une température de 25–35°.

De la solution obtenue, quelques feuilles d'une couleur jaunâtre se cristallisent, ces feuilles sont impurifiées par quelque petite quantité de sélénium élémentaire. Ce précipité est séparé de la solution benzénique par filtrage à travers d'une plaque de verre, on le lave ensuite avec du benzène; facilement on le purifie par dissolution en acétone et cristallisation de la solution filtrée.

#### *Rendement*

Celui que nous avons obtenu dans la préparation de ce composé, s'élève à un 20% (la moyenne d'un grand nombre de préparations). Mais dans les eaux mères, on peut obtenir encore quelques petites quantités du produit, quoique moins pures, mais qui élèvent encore le rendement obtenu.

#### *Propriétés*

Le point de fusion est de 210°, un peu plus élevé de celui que nous donne CORNELIUS[3] pour la sélénodiphénylamine (195°). Nous avons constaté la présence de chlore dans la molécule et l'analyse quantitative a mis en évidence l'existence de la sélénodiphénylamine monochlorés. Les résultats obtenus dans l'analyse élémentaire sont donnés dans le Tableau I.

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* Avec MELIAN, nous avons pu obtenir dans nos laboratoires la *sélénodiphénylamine* en employant $Se_2Cl_2$, dont les propriétés analytiques sont actuellement en étude (Communication privée).

TABLEAU I

| *Trouvé* | *Calculé pour la chlorosélénodiphénylamine* |
|---|---|
| 49.22% C | 51.30% C |
| 4.28% N | 4.90% N |
| 2.74% H | 2.80% H |

Il n'a pas été possible d'établir avec exactitude la position du chlore dans la molécule; il est probable que les composés isomères avec le chlore en position *ortho* et *para*, par rapport au groupe NH prédominent.

La monochlorosélénodiphénylamine est soluble dans un grand nombre de dissolvants organiques: acétone, benzène, chloroforme, dioxène, glycol, etc. Elle est peu soluble dans les alcools éthyliques et méthyliques, mais sa solubilité peut atteindre un 0.1%, ce qui permet d'obtenir des solutions de cette concentration. Elle est tout à fait insoluble dans l'eau. Cette propriété énumerée en dernier lieu est très importante à considérer en analyse car on peut arriver à l'insolubilisation du réactif quand les solutions organiques de celui-ci, sont ajoutées aux solutions aqueuses des cations. Cependant la solution acétonique à 0.2% du réactif, admet jusqu'à un 70% d'eau sans précipiter, mais il est convenable de déterminer empiriquement dans chaque cas, la limite possible de dilution.

Ces solutions sont d'une couleur jaune clair et sont assez stables. Les solutions du réactif en chloroforme, acétone, alcool et d'autres, deviennent verdâtres par l'action du temps, mais elles gardent leur réactivité en ce qui concerne le palladium et d'autres cations. Il s'agit d'une oxydation produite et accélérée par la lumière du jour. Dans tous les cas, on peut les conserver assez de temps sans modifications sensibles.

## COMPORTEMENT DE LA MONOCHLOROSÉLÉNODIPHÉNYLAMINE COMME RÉACTIF QUALITATIF

(*1*) La monochlorosélénodiphénylamine est un réactif spécifique du palladium. Une solution diluée de $PdCl_2$ dans un milieu HCl faible (un excès de HCl est gênant) avec la solution acétonique du réactif à 0.1–0.2%, et en présence d'un excès d'acétone, donne une coloration violette semblable à celle du $KMnO_4$ dilué. Si on dilue cette solution avec de l'eau, la couleur tourne à un bleu intense, et si la dilution est suffisante, on obtient un précipité bleu foncé. S'il y a un excès de réactif, la couleur apparaîtra plus claire*.

(*2*) Avec une solution alcoolique, en présence d'un excès d'alcool, le réactif donne avec le palladium(II) une coloration bleue. Cette coloration bleue ou violette n'est donnée que par le palladium(II) dans un milieu HCl faible. Dans le même solvant, avec platine(V) et osmium(VIII) on n'obtient pas de réaction.

(*3*) La monochlorosélénodiphénylamine est dissoute dans les acides $HNO_3$, $HClO_4$ et $H_2SO_4$ avec une coloration rouge sang, mais ces acides en petite quantité ne prètent aucune coloration au réactif.

(*4*) La réaction du palladium n'a lieu ni dans un milieu ammoniacal ($(NH_4)_2CO_3$

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* La couleur du complexe monochlorosélénodiphénylamine–palladium dépend donc du rapport solvant organique: eau; il faudra avoir soin de cette propriété dans l'étude spectrophotométrique du composé.

empêche aussi cette réaction), ni dans un milieu cyanuré. Quand le réactif est ajouté à une solution ammoniacale, la réaction n'apparaît pas, mais si on ajoute un excès de HCl, la réaction se produit avec une sensibilité plus petite. On déduit de celà que le complexe ammoniacal du palladium formé, est peu ionisé.

(5) Avec les oxydants fer(III), argent, thallium(III), permanganate, or(III), chromate (à 0.1% et dans un milieu neutre ou faiblement acide), une coloration verte émeraude est obtenue; la coloration dépend donc des concentrations du réactif et de l'oxydant, que l'action du temps transforme en un précipité vert foncé.

(*6*) Dans tous les essais on a employé une solution acétonique du réactif à 0.2%.

(7) Les cations suivants ne donnent aucune réaction dans les solutions à 1% du cation: Li, Na, K, $NH_4^+$, Ca, Sr, Ba, Mg; ni les ions Cu(II), Hg(II), Pb, Cd, Bi, As(III), Sb(III), Sn(II), Ni, Co, Mn, Al, Th, W(VI), $UO_2$, Pt(IV), La(III), Se(IV) en solution à 0.1% du cation métallique. Les solutions qui, comme celles du Sn(II) et Sb(III) renferment une quantité de HCl libre, donnent une coloration rosée, produite par la présence de HCl concentré. Les essais sont effectués sur la plaque au touche (goutte) entre trois gouttes de la solution de cation et trois gouttes de celle du réactif en acétone à 0.2%. Dans le tube à essai, on peut opérer avec des quantités doubles.

### *Sensibilité de la réaction avec le palladium(II)*

Nous avons préparé des solutions de palladium(II) à 0.1, 0.01 et 0.001% et nous avons opéré avec celle du réactif en acétone à 0.2%. Dans les deux premières la réaction est très intense et dans la troisième, que nous avons fait avec deux gouttes de palladium et trois du réactif dans un petit tube à essai, la réaction est clairement positive. Il a été ainsi décelé 1 $\mu g$ de palladium dans 0.25 ml de volume final. Limite de dilution $4 \cdot 10^{-6}$; p$D$ = 5.4. Dans la plaque et sur le papier filtre, la sensibilité est du même ordre. Pour les essais sur papier il faut laisser sécher le papier.

De tous les composés organiques du sélénium employés comme réactifs et préparés jusqu'à présent par nous mêmes, dans nos laboratoires, *celui-ci apparaît comme le plus sensible et comme le plus spécifique du palladium.*

### *Formule du composé résultant de la réaction entre le palladium et la monochlorosélénodiphénylamine*

Nous avons observé qu'en diluant la solution acétonique du composé organique soluble du palladium, un précipité bleu foncé s'est formé. Ce précipité est souvent accompagné par un excès de réactif insolubilisé, en même temps par l'action de l'eau; cette insolubilisation peut être empêchée en faisant la précipitation dans un milieu riche dans le solvant organique et par un lavage répété du précipité avec de l'alcool. Le précipité qui est très stable, peut être séché dans l'étuve à 110° sans subir aucune altération. Qualitativement il est très facile de constater dans le composé la présence du:

*Palladium.* Après avoir détruit la matière organique par un mélange des acides nitrique et perchlorique, et chassé l'excès d'acide, le palladium est précipité par la diméthylglyoxime.

*Sélénium.* Dans la solution provenant de la séparation du complexe Pd-diméthylglyoxime, ajouter du sulphate d'hydrazine ou du chlorhydrate d'hydroxylamine, le sélénium qui s'y trouve se réduit et forme un précipité d'une couleur rouge, qui lui est caractéristique.

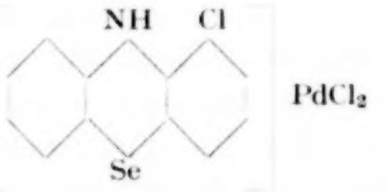
*Chlore.* La substance placée dans une spatule en cuivre est portée à un bec de lampe. La flamme lui fait prendre une coloration verte très intense, ce qui indique la présence de chlore.

L'analyse élémentaire quantitative du complexe du palladium et la monochlorosélénodiphénylamine est représentée dans le Tableau II.

TABLEAU II

| | *Trouvé* % | *Calculé pour la ($C_{12}H_8NSeCl$) $PdCl_2$* % |
|---|---|---|
| Carbone | 38.9 | 39.0 |
| Azote | 3.6 | 3.8 |
| Hydrogène | 2.4 | 2.2 |
| Chlore | 20.5 | 19.2 |
| Palladium | 13.5 | 14.4 |

Tenant compte des complexes que le palladium forme avec les autres composés organiques aminés on peut attribuer au composé que nous avons préparé, pour la première fois, la formule suivante condensée:



La position de l'halogène n'est pas certaine, parce qu'elle est très difficile à signaler. Il s'agira probablement d'un mélange d'isomères. Nous poursuivons l'étude structurale de ce complexe métallique et nous continuons aussi l'étude spectrophotométrique de cette nouvelle réaction analytique du palladium(II).

## RÉSUMÉ

Poursuivant nos études sur l'application des composés organoséléniques, nous proposons dans ce travail la monochlorosélénodiphénylamine comme un nouveau réactif du palladium, d'une grande sensibilité et d'une excellente sélectivité. La formule du composé obtenu est analysée.

## SUMMARY

Studies on the application of organoselenium compounds have been continued. Monochloroselenodiphenylamine is suggested as a new sensitive and selective reagent for palladium; the complex obtained has been analysed.

## ZUSAMMENFASSUNG

Studien über die Anwendung von organoselenium Gemischen wurden fortgesetzt. Monochloroselenodiphenylamin wird als ein selektives und sensitives Reagens für Palladium empfohlen. Der erhaltene Komplex wurde analysiert.

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# THE EFFECT OF ORGANIC SUBSTITUENTS AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS ON THEIR EXTRACTION ABILITIES FOR URANIUM

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(Received January 17th, 1961)

## INTRODUCTION

Recent studies have reported the development of many organophosphorus solvents for the processing of ores and spent fuels[1-5]. Of the organophosphorus compounds, tri-*n*-butyl phosphate (TBP) is well-established as an extracting solvent for uranium, thorium and many other elements, and its extraction properties have been extensively studied[6-13]. Recently the study has been extended to other phosphorus-containing solvents which exhibit better extraction properties than TBP[14,15]. Despite the increasing analytical value of organophosphorus compounds, much must still be done fully to elucidate the extraction properties of solvents. Of the numerous extractions possible with organophosphorus solvents, the extraction of uranium is one of the most important. The present article is intended to present comprehensive data which illustrate the effect of the organic substituents and the solvent structure upon the extraction of uranium from nitric acid media. Firstly, the effect of the organic substituents was studied with a series of twelve phosphates, and secondly, the effect of the structure change was studied with a series of phosphates, phosphonate, phosphinate and phosphine oxide with similar alkyl groups.

## EXPERIMENTAL

### *Reagents*

*Uranium.* Reagent grade uranyl nitrate (British Drug Co.) was used after recrystallization from water. All the uranyl nitrate stock solutions were prepared in the nitric acid solutions of different concentrations.

*Organophosphorus solvents.* The organic phosphorus compounds employed included the following: *Phosphates* with normal alkyl groups — triethyl phosphate, tri-*n*-propyl phosphate, tri-*n*-butyl phosphate and tri-*n*-octyl phosphate. *Phosphates* with branching alkyl groups — triisopropyl phosphate, triisobutyl phosphate, tri-*sec*-butyl phosphate, triisoamyl phosphate, tris-(2-ethylhexyl) phosphate and tricyclohexyl phosphate. *Phosphates* with aryl groups — triphenyl phosphate, tris-(2-methylphenyl) phosphate and tris-(4-methylphenyl) phosphate. *Phosphonate* — diethylbutyl phosphonate. *Phosphinate* — tri-*n*-butyl phosphinate and *n*-butyl-di-*n*-butyl phosphinate. *Phosphine oxide* — tri-*n*-butyl phosphine oxide.

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All the organophosphorus solvents were synthesized by Tama Chemicals, Tokyo, Japan, and the solvents were in most cases purified by vacuum distillation For tri-*n*-butyl phosphate and tri-*n*-propyl phosphate, repeated washing with sodium bicarbonate and distilled water was carried out as well as the subsequent vacuum distillation. Both triphenyl phosphate and tris-(4-methylphenyl) phosphate were purified by recrystallization from benzene. All the solvents were diluted with carbon tetrachloride and stored in brown bottles in a refrigerator. Other chemicals employed were of reagent grade. Carbon tetrachloride was purified by distillation.

### *Procedure*

All the phosphorus solvents were dissolved in carbon tetrachloride at concentrations of 0.732 *M*. The concentrations of the uranyl nitrate stock solutions were 0.1 and 0.01 *M* in 1, 3, 5, 7, 10 and 13 *M* nitric acid.

5 ml each of uranyl nitrate solution and solvent were placed in a measuring flask and shaken in a thermostated bath for about an hour to reach equilibrium. The solvent was not pre-equilibrated with nitric acid. Both the uranium and nitric acid contents in the aqueous phase were determined before and after the equilibration, and then the amounts of uranium and nitric acid extracted into the organic phase were indirectly calculated. For the determination of nitric acid, ordinary titration with *N* sodium hydroxide solution was applied after precipitation of uranium with hydrogen peroxide; the hydrogen ion liberated by the uranium precipitation was corrected for. Uranium content was determined colorimetrically by the hydrogen peroxide method, the absorbance being measured at 400 m$\mu$.

The calculated distribution ratio, $K_d$, serves as a measure of the extracting ability of the solvent.

## RESULTS AND DISCUSSION

### *Mechanism of extraction*

For the extraction of uranium by TBP, it was demonstrated that the reaction proceeded as follows[1,6,13]:

$$UO^{+2}_{2(aq.)} + 2NO^{-}_{3(aq.)} + 2\,TBP_{(org)} \rightleftarrows [UO_2(NO_3)_2(TBP)_2]_{(org)}$$

For the phosphates, diethylbutyl phosphonate and tri-*n*-butyl phosphine oxide tested, the above extraction reaction was (except for triphenyl phosphate, tris-(2-methylphenyl) and tris-(4-methylphenyl) phosphates which did not show any appreciable extracting abilities) confirmed by the determination of both solvent and acid dependences, as well as by the determination of the solubility of uranyl nitrate into the organic phase, which was saturated at the ratio of 1 : 2 (U : solvent).

### *Distribution ratios*

(*1*) Extraction by phosphates with normal alkyl groups. The extraction curves with the normal alkyl phosphates are shown in Fig. 1. The $K_d$ values are slightly increased when the alkyl group is replaced by a higher chain. The exceptions to this are triethyl phosphate and tri-*n*-propyl phosphate.

(*2*) Extraction by phosphates with branching alkyl groups. The branching effect of alkyl substituents was studied by means of a comparison of the distribution ratios

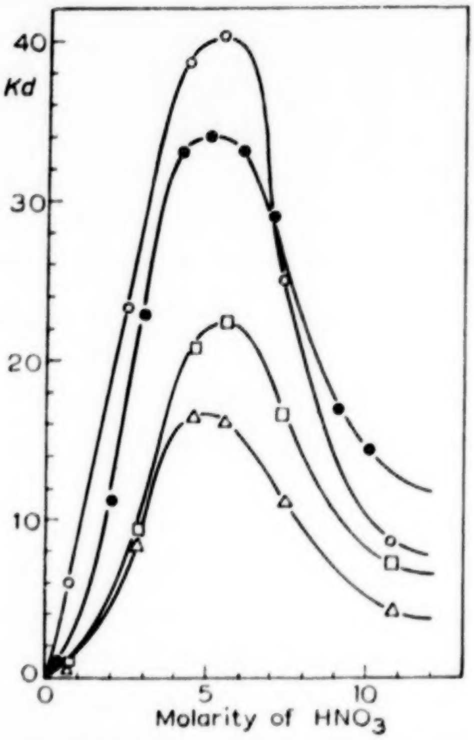

Fig. 1. Extraction curves with normal alkyl phosphates. Initial solvent: 0.732 *M*, $UO_2(NO_3)_2$: 0.01 *M*. □ triethyl; △ tri-*n*-propyl; ● tri-*n*-butyl; ○ tri-*n*-octyl; *t* = 25°.

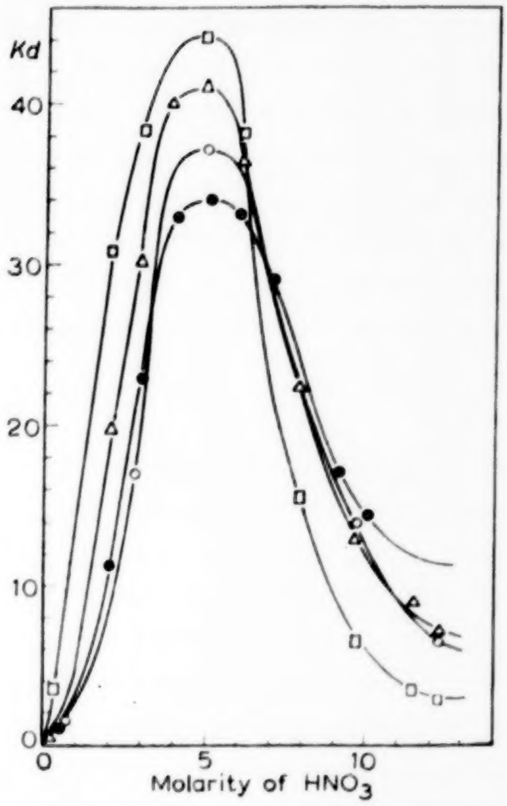

Fig. 2. Extraction curves with branching alkyl phosphates. Initial solvent: 0.732 *M*, $UO_2(NO_3)_2$: 0.01 *M*. □ tri-*sec*-butyl; △ triisopropyl; ○ triisobutyl; ● tri-*n*-butyl; *t* = 25°.

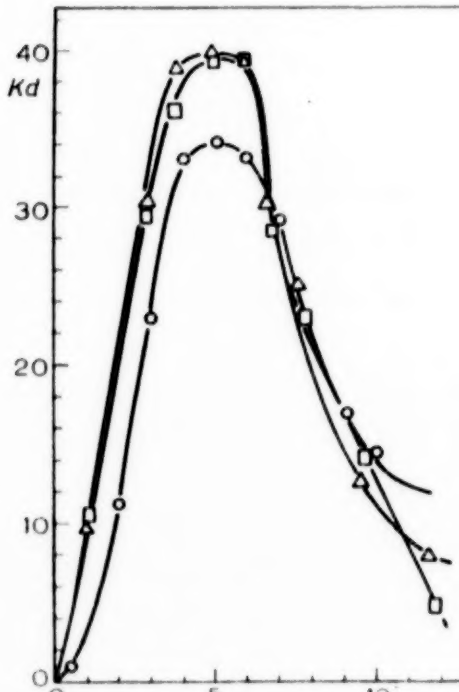

Fig. 3. Extraction curves with branching alkyl phosphates. Initial solvent: 0.732 *M*, $UO_2(NO_3)_2$: 0.01 *M*. □ tris-(2-ethylhexyl); △ triisoamyl; ○ tri-*n*-butyl; *t* = 25°.

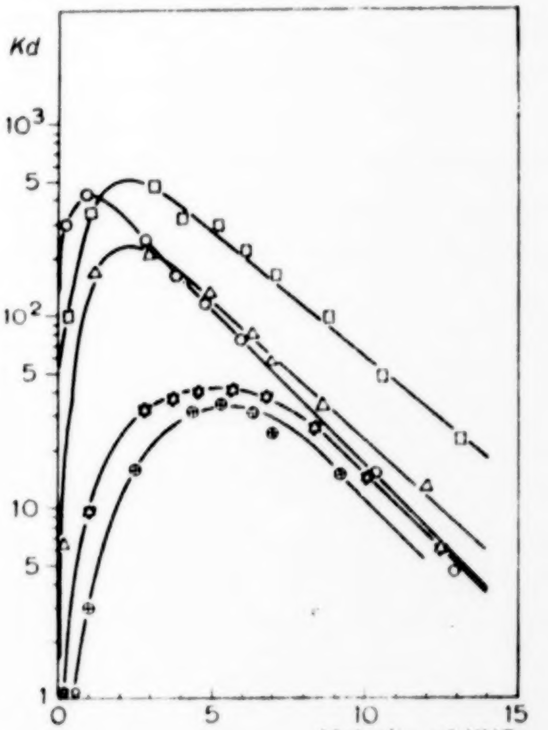

Fig. 4. Extraction curves with phosphine oxide, phosphinate, phosphonate, tricyclohexyl and tri-*n*-butyl phosphate. Initial solvent: 0.732 *M*, $UO_2(NO_3)_2$: 0.1 *M*. ⊕ tri-*n*-butyl phosphate; △ tricyclohexyl phosphate; □ tri-*n*-butyl phosphinate; ○ tri-*n*-butyl phosphine oxide; ✫ diethylbutyl phosphonate; *t* = 25°.

of triisopropyl phosphate, triisobutyl phosphate, tri-*sec*-butyl phosphate, triisoamyl phosphate and tris-(2-ethylhexyl) phosphate and is shown in Figs. 2 and 3 with the reference extraction curve obtained with tri-*n*-butyl phosphate. The branching of the alkyl group results in a definite increase in $K_d$ values, and the effect of branching becomes more apparent at the carbon closest to the alkoxyl oxygen. Highly branched tricyclohexyl phosphate shows an unusually high extracting ability (see Fig. 4). The high extracting ability of triisopropyl phosphate has also been reported[16].

(*3*) Extraction by the phosphonate, phosphinate and phosphine oxide. The extraction curves with diethylbutyl phosphonate, *n*-butyldibutyl phosphinate and tri-*n*-butyl phosphine oxide are shown in Fig. 4. As is evident, higher distribution ratios are observed with the phosphonate, phosphinate and phosphine oxide than with most phosphates. A close similarity is observed among the extraction curves of diethylbutyl phosphonate and most phosphates with the existence of the maximum $K_d$ value around 5 $M$ nitric acid. Tricyclohexyl phosphate is an exception in this case. *n*-Butyldibutyl phosphinate, tri-*n*-butyl phosphine oxide* and tricyclohexyl phosphate show similar extraction curves in which the maximum $K_d$ appears at 1 $M$ nitric acid.

The existence of a maximum $K_d$ value on the extraction curves is interpreted as a result of competition between uranium and nitric acid[13]. With the increase in the affinity of nitric acid towards the solvents, the position of maximum $K_d$ shifts to a lower nitric acid concentration.

In Table I, the data of the distribution ratios at the major nitric acid concentrations are listed for all the organophosphorus solvents tested. As is evident, the relative order of the extracting abilities is tri-*n*-butyl phosphine oxide and *n*-butyldibutyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups; this is in good agreement with already published data[14,15,17].

TABLE I

SUMMARY OF $K_d$ VALUES

Solvent: 0.732 $M$. Initial $UO_2(NO_3)_2$: 0.01 $M$. $t = 25°$

| *Solvent* | *$HNO_3$ aq* | | | | | | |
|---|---|---|---|---|---|---|---|
| | *1 M* | *3 M* | *5 M* | *6 M* | *8 M* | *10 M* | *12 M* |
| Tri-*n*-ethyl phosphate | 1.7 | 11.1 | 22.1 | 22.0 | 13.9 | 8.5 | 6.5 |
| Tri-*n*-propyl phosphate | 1.4 | 9.9 | 16.7 | 15.2 | 9.4 | 5.3 | 3.8 |
| Tri-*n*-butyl phosphate | 3.1 | 23.7 | 33.9 | 33.2 | 18.7 | 9.6 | 7.8 |
| Tri-*n*-octyl phosphate | 8.5 | 29.2 | 40.1 | 39.4 | 21.8 | 14.4 | 11.8 |
| Triiso-propyl phosphate | 4.9 | 32.9 | 41.0 | 36.7 | 21.2 | 13.8 | 7.6 |
| Triiso-butyl phosphate | 3.0 | 21.3 | 37.2 | 35.5 | 21.4 | 14.0 | 7.0 |
| *Sec*-butyl phosphate | 15.1 | 39.5 | 44.2 | 37.2 | 14.5 | 6.0 | 3.1 |
| Triisoamyl phosphate | 9.0 | 33.0 | 39.6 | 39.0 | 19.3 | 11.0 | 7.5 |
| Tris-(2-ethylhexyl) phosphate | 9.0 | 31.1 | 39.4 | 38.2 | 21.0 | 12.4 | 4.1 |
| Tricyclohexyl phosphate | 133 | 235 | 218 | 120 | 62 | 23.0 | 11.5 |
| Diethylbutyl phosphonate | 9.7 | 27.5 | 33.5 | 40.8 | 38.0 | 14.7 | 7.4 |
| Tri-*n*-butyl phosphinate | 350 | 520 | 480 | 290 | 155 | 63 | 35 |
| Tri-*n*-butyl phosphine oxide | 440 | 340 | 230 | 108 | 51 | 16.9 | 7.9 |

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* Above 6 $M$ nitric acid, a third phase containing a little uranium appeared. For the calculation of the $K_d$ values the existence of this third phase was ignored.

Triphenyl phosphate and tris-(2-methylphenyl) and tris-(4-methylphenyl) phosphate demonstrate no appreciable extraction properties; the introduction of the electronegative group nearly destroyed the solvent strength[14]. It can be concluded that organic substituents attached to the phosphoryl group affect the electronegativity of the phosphoryl oxygen as well as the affinity of the solvent for the aqueous phase. Any substituent or change in the solvent structure which enhances the electronegativity of the phosphoryl oxygen results in higher $K_a$ values. The introduction of branching alkyl groups, as well as the removal of the alkoxyl oxygen, definitely enhances the extracting ability. It was observed among the phosphates tested that the maximum $K_a$ values are inversely proportional to the acid dissociation constant of the corresponding carboxylic acid. It is evident that a small acid dissociation constant refers to a large electron donor ability which in turn increases the electron cloud density of the phosphoryl oxygen. Ref.[18] demonstrates that the introduction of groups such as hydroxyl, chloro, or bromo results in an increased acid dissociation constant which decreases the electronegativity of the phosphoryl oxygen. The increase in the $K_a$ value by the introduction of branching alkyl groups or the elimination of the extraction property by the introduction of aryl groups can be interpreted on the basis of the electron donor or electron sink property of the organic substituent. BURGER[14,17], however, has reported that the introduction of the phenyl group which is bound directly to the phosphorus atom does not eliminate the extracting ability. This fact can be interpreted qualitatively as the result of a conjugation between the phenyl group and phosphoryl oxygen through the phosphorus atom. Also a direct bond between the alkyl and phosphoryl groups should result in an increase in the electron cloud density of the phosphoryl oxygen owing to the elimination of the electron sink property of the alkoxyl oxygen, thus a higher extracting ability can be expected in phosphonate, phosphinate and phosphine oxide than in most phosphates. The equilibrium constant $K$ $(\mathrm{mol/l})^{-4}$ and the free energy change $\Delta F$ (kcal/mol) calculated according to equation (1) are: 19.3 and $-1.8$ for tri-*n*-butyl phosphate, 760 and $-4.0$ for diethylbutyl phosphonate and $2.5 \cdot 10^6$ and $-8.8$ for tributyl phosphine oxide. These thermodynamic quantities are in good agreement with the order of extracting abilities of the solvents*. At the same time SIDDALL[19] has reported that a nearly constant entropy change $\Delta S$ is observed throughout many phosphates and phosphonates tested.

As the enthalpy change $\Delta H$ relates to the binding energy between the solvent and uranium, the effect of an organic substituent on the solvent is interpreted by the nature of the electron density of the phosphoryl oxygen which is the bonding center of solvent to uranium. Another influence, the affinity of the solvent for the aqueous phase, is demonstrated in the solubilities of the phosphorus compounds to water. Among the phosphates with normal alkyl groups, trimethyl phosphate is completely miscible with water, as is triethyl phosphate, but the latter becomes immiscible if the solvent is diluted with, for example, carbon tetrachloride or kerosene. Phosphates above tripropyl phosphate are immiscible with water. Phosphates with branching alkyl groups are more soluble in water than phosphates with normal alkyl groups. It has been demonstrated that the solubility of tri-*sec*-butyl phosphate is nearly three times higher than that of tri-*n*-butyl phosphate[20]. Among the phosphate, phosphonate, phosphinate and phosphine oxide with similar alkyl groups, the relative order of the affinity for the aqueous phase is phosphine oxide > phosphinate > phosphonate > phosphate, and is probably due to an increase in the dipole moment of the solvent as well as the ability to complex water. The shift of the $P = O$ stretching frequency (1280 $cm^{-1}$) and the splitting of the nitrate degenerate frequency (1380 $cm^{-1}$) in the infrared spectra of metal-TBP complexes[21,22] indicate that in the metal nitrate-TBP complexes, those ligands are bound to metal atoms through oxygen atoms. The effects of organic substituents in the organophosphorus solvents and the infrared results suggest that the extraction process may be explained by the organic electron theory and acid-base concept, as well as by the solubility and stability of complex in the solvent.

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* Those $K$ values were obtained by the usual method of extrapolating the root of the ionic strength to zero with a correction for aqueous nitrate ion activity.

## ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Drs. KENJIRO KIMURA, TAKASHI MUKAIBO, KEICHI OSHIMA AND KEIJI NAITO, and to Prof. SHOJI MAKISHIMA for their suggestions and encouragement. They are also grateful to Mr. RYOICHI UEHARA of Tama Chemical Co. for his synthesis of organophosphorus solvents, and to Messrs. TOSHI SUZUKI AND HIROKAZU UMEZAWA for their assistance.

## SUMMARY

With 12 phosphates, 1 phosphonate, 1 phosphinate and 1 phosphine oxide, the pattern of uranium extraction from nitric acid media was investigated. The extraction was affected by the nature of the organic substituents attached to the phosphoryl group as well as by the solvent structure. Phosphates with aryl groups were not satisfactory extractants. The extraction ability increased as the alkyl group was made larger; phosphates with branching alkyl groups were better than phosphates with normal alkyl groups. Removal of the alkoxyl oxygen enhanced the extracting abilities. The relative order of the extracting abilities were: tri-*n*-butyl phosphine oxide and tri-*n*-butyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate > phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups.

## RÉSUMÉ

Les auteurs ont examiné l'influence de substituants organiques et de la structure de divers composés organophosphorés sur l'extraction de l'uranium. Les composés avec groupements alcoylés ramifiés, tels que l'oxyde de tri-*n*-butylphosphine et le tri-*n*-butylphosphinate, ont donné les meilleurs résultats.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss der Struktur und verschiedener organischer Substituenten bei organischen Phosphorverbindungen als Extraktionsmittel für Uran. Langkettige und verzweigte Alkylgruppen ergeben eine bessere Extraktionswirkung.

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# HYDRAZINE AS A GENERAL TITRIMETRIC REAGENT IN IODIMETRY

## PART II

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We have already discussed[1] the preparation, standardisation and stability of hydrazine solution and its use for the determination of iodine liberated from hydriodic acid or potassium iodide by inorganic oxidants or of excess iodine after the oxidation of inorganic reductants. The work has now been extended for the determination of several organic compounds which are known to react quantitatively with iodine according to some definite reaction. These include carbonyl compounds[2,3], sulphydryl compounds[4], phenols[5], carbohydrates[3], and certain nitrogen[6] and sulphur[7] compounds.

### EXPERIMENTAL

Standard hydrazine solution (0.1 *N*) was prepared by direct weighing of analytical grade hydrazine hydrochloride as already described[1] and its strength was checked with previously standardised iodine solution.

### *General method for titrating excess iodine*

The compound under study was mixed with an excess of iodine solution in acidic or alkaline medium and allowed to stand for a definite time. Sufficient sodium bicarbonate was then added to neutralise any free mineral acid present and to adjust the pH of the solution to 7–7.5. The excess iodine was then titrated with a standard hydrazine solution by the usual starch-iodine or starch glycollate method or by the potentiometric dead-stop technique.

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In the case of aldehydes, the studies were also extended to the formation of addition compounds with sodium bisulphite, the excess of bisulphite being reacted with a known amount of iodine solution which was back-titrated. Both the methods, *i.e.* the direct reaction of aldehydes and iodine and the addition compound formation with bisulphite, gave identical and reproducible results.

### *Carbonyl compounds*

The compounds studied were formaldehyde, acetaldehyde, benzaldehyde and acetone.

To 10 ml of a 0.05 *M* solution of the compound about 5 ml of 4 *N* sodium hydroxide and 25 ml of 0.1 *N* iodine solution were added. The mixture was shaken and allowed to stand for 5–15 min depending on the compound. The reaction mixture was acidified to liberate iodine from hypoiodite, the free acid was neutralised with sodium bicarbonate and the titration was carried out with hydrazine solution.

### *Chloral hydrate*

To 25 ml of 0.1 *N* iodine solution were added 20 ml of 4 *N* sodium carbonate and 10 ml of 0.1 *N* chloral hydrate solution. The flask was stoppered and allowed to stand for 1 h. The unused iodine was then liberated by acidification and titrated after neutralisation of the free acid.

### *Thiourea and xanthates*

To a solution containing about 0.02 g of thiourea or xanthate, 25 ml of 0.1 *N* iodine solution was added and allowed to stand for 5 min; 10 ml of 10% potassium hydroxide was then added and the reaction mixture set aside for 10 min and then acidified; excess iodine was back-titrated after neutralisation. The results are reproducible to ±0.5%.

### *Nitrogen compounds*

To 20 ml of 0.5 *M* phosphate buffer solution of pH 7 sufficient iodine solution was added so that after reaction an excess of about 5 ml was present. The semicarbazide solution was added and excess iodine was back-titrated as usual.

The method was found to be satisfactory for the determination of thiosemicarbazide provided that the reaction mixture was allowed to stand for about 30 min.

### *Sulphydryl compounds*

Compounds such as thioglycollic acid, cystine and glutathione can be directly titrated with iodine solution but atmospheric oxidation of these compounds may occur so the method involving excess iodine is to be preferred. A known amount of the substance under study was added to excess iodine solution and after standing for some time excess iodine was titrated as described earlier.

### *Resorcinol and hydroquinone*

To a solution containing about 0.05 g of resorcinol was added 50 ml of acetate buffer solution followed by 50 ml of 0.1 *N* iodine solution and excess iodine was back-titrated after 1 min.

In the case of hydroquinone, the reaction mixture was allowed to stand for 5 min and then titrated. The results are reproducible to ±0.3%.

### *Phenolphthalein*

To an aqueous alkaline solution of *ca.* 50 mg of phenolphthalein about 20 ml of 0.1 *N* iodine solution was added and the mixture was allowed to stand for 2 h. The excess alkali was then neutralised and iodine determined.

### *Isonicotinic acid hydrazide*

To 25 ml of the solution containing about 2 g of the hydrazide per litre were added 1 g of sodium bicarbonate, 25 ml of water and 25 ml of 0.1 *N* iodine solution. After 15 min the excess iodine was titrated.

### *Ascorbic acid*

To 25 ml of 0.1 *N* ascorbic acid solution were added 4 ml of 10 *N* sulphuric acid and 20 ml of 0.1 *N* iodine solution. The reaction mixture was allowed to stand for about 1 min, 3 ml of starch were added and the titration was carried out after neutralisation.

### *Theobromine*

0.15–0.2 g of theobromine was dissolved in 4 ml of *N* sodium hydroxide and the solution was acidified with 15 ml of 4 *N* hydrochloric acid; 6 g of sodium chloride was then added and after dissolution was complete, the solution was diluted to 100 ml and filtered. An aliquot of the filtrate was directly titrated with the hydrazine solution in the presence of a slight excess of sodium bicarbonate.

The method has been extended for the determination of antipyrine and atophan.

### *Aldoses*

To 10 ml of 0.05 *M* aldose solution, 25 ml of 0.1 *N* iodine solution and 15 ml of sodium carbonate solution were added and the reaction mixture was allowed to stand for about 30 min before the usual titration of excess iodine.

Satisfactory results were obtained in the case of glucose, galactose, maltose, lactose, rhamnose and arabinose.

### *Bisulphite method for aldehydes*

To an aldehyde solution a 30–50% excess of bisulphite solution containing 5% alcohol was added and the mixture was set aside for 30 min to allow the formation of the addition product. It was then mixed with 25 ml of 0.1 *N* iodine solution and excess iodine was back-titrated.

The method gave good results in the case of formaldehyde, acetaldehyde and benzaldehyde.

## DISCUSSION

As expected, the reaction products of many organic compounds do not interfere in the hydrazine-iodine reaction and therefore the method can be extended conveniently for the back-titration of iodine after the oxidation or iodination of such compounds. The usual advantages of hydrazine over thiosulphate which were observed in the determination of inorganic compounds are also apparent in the determination of organic compounds.

## SUMMARY

The general method involving hydrazine as a substitute for thiosulphate in iodimetry has been extended for the determination of organic compounds containing carbonyl, phenolic and sulphydryl groups and for some sulphur- and nitrogen-containing compounds and aldoses.

## RÉSUMÉ

Les auteurs ont appliqué la méthode iodométrique générale, substituant l'hydrazine au thiosulfate, au dosage de divers composés organiques (composés avec groupements =CO,—OH,—SH; composés sulfurés et azotés; aldoses).

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung von Hydrazinsulfatlösung an Stelle von Thiosulfat bei der jodometrischen Bestimmung organischer Verbindungen.

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# SEPARATION OF URANIUM BY ANION EXCHANGE

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(Received January 10th, 1961)

## INTRODUCTION

Previous research work on ion exchange in mixed solvents[1-8] has shown that uranium as well as thorium is efficiently retained on anion exchangers of the strongly basic type from mixtures of aliphatic alcohols and mineral acids. It has also been found that the strength of adsorption of uranium as a negatively charged chloride complex increases with growing chain length of the alcohol and increase in acid normality[8]. Similar results were obtained with thorium and vanadium[9].

The present method is our extension of previous research work (carried out in ethanolic medium) on the separation of uranium from nearly all elements[6]. Here we examine in detail the use of a methanol–hydrochloric acid mixture in which the distribution coefficient of uranium is still suitably high, whereas the distribution coefficients of the elements to be separated from uranium are correspondingly low so that a quantitative separation can be effected. For this purpose a mixture consisting of 80% methanol and 20% 6 *N* hydrochloric acid was selected. In this medium the addition of ascorbic acid causes the adsorption of some elements which must be separated from uranium, to be further reduced. For example, the elements, iron, nickel, cobalt and copper are not retained by the resin although they would be if the reducing agent were absent. This effect of ascorbic acid decreases with increasing chain length of the alcohol, so that methanol in combination with 6 *N* hydrochloric acid is the most suitable solvent. However, the percentage of methanol must not differ much from 80%; at higher alcohol concentrations ascorbic acid is less effective and other elements are partially coadsorbed and cannot easily be washed out, whereas at lower concentrations the distribution coefficient of uranium is correspondingly smaller.

## REAGENTS

The resin used for the separation experiments and equilibrium studies was Dowex 1 X 8 (100–200 mesh, chloride form). The resin was soaked in a solution of 80% (v/v) methanol and 20% 6 *N* hydrochloric acid and was subsequently transferred to the ion exchange column, taking care that no air bubbles were introduced in the resin bed. For the determination of the distribution coefficients the air-dried form of the resin was used. Standard solutions of uranium and of other elements investigated were prepared by dissolving reagent grade chlorides of these elements in 6 *N* hydrochloric acid. The methanol–hydrochloric acid solution mentioned above was also used to wash the columns (wash solution). Further reagents were pure methanol, pure ascorbic acid (Wiener Heilmittelwerke), 6 *N* hydrochloric acid and 0.01 *N* nitric acid.

## APPARATUS

The columns employed were of the same type and dimensions as earlier described[10]. For the polarographic determination of uranium a Sargent, model XXI polarograph was used[11].

## PROCEDURE

*Separation of uranium from thorium, zirconium, iron, cobalt, nickel, aluminium, etc.*

*Pretreatment of the resin bed.* After the resin had been transferred to the ion exchange column as described above, it was treated with 50 ml of the wash solution. If the sample contains iron, cobalt, nickel or copper, the wash solution as well as the sample solution must contain ascorbic acid (about 4 g/100 ml solution).

*Sorption step.* The sample solution consisted of 80 ml of methanol and 20 ml of 6 *N* hydrochloric acid containing a known amount of uranium, a definite quantity of the element from which uranium was to be separated, and, if any of the above-mentioned elements were present, about 4 g of ascorbic acid added in portions. This solution was passed through the column at a flow rate of less than 50 ml/h. The uranium was thus adsorbed on the resin whereas most of the other elements passed into the effluent.

*Washing and elution.* After complete sorption the resin was washed with 150 ml of the wash solution in portions. Misleading results may be obtained if all the wash solution is added together. Washing with ascorbic acid-containing washing solution was necessary when one of the above-mentioned elements was present; the resin was then washed with about 50 ml of the wash solution (containing no ascorbic acid) in order to remove ascorbic acid. Afterwards the uranium was eluted by passing 100 ml of 1 *N* hydrochloric acid through the column.

*Determination of uranium in the eluate.* An aliquot of the eluate containing not more than 5 $\mu$g of uranium was transferred to a quartz dish and evaporated to dryness on a water bath. The dish was then briefly ignited in order to destroy organic matter. The residue was dissolved in about 10 ml of 6 *N* hydrochloric acid and the solution was evaporated to dryness on the water bath. Then 10 ml of 0.01 *N* nitric acid were added and the polarographic determination by means of the catalytic nitrate wave was carried out as earlier described[11].

## RESULTS AND DISCUSSIONS

The results of a series of separation experiments by the above procedure are recorded in Table I. It can be seen that uranium was separated quantitatively from all the elements examined *i.e.* the eluates were free of the elements used.

Of the elements recorded in Table I, lead and bismuth, like uranium, were strongly adsorbed on the resin. Their adsorption could not be decreased by addition of ascorbic acid. However, uranium was easily separated from these elements during the elution step with 1 *N* hydrochloric acid, when uranium was eluted while both bismuth and lead remained strongly adsorbed on the lower part of the resin as their chloride complexes. Bismuth could be removed from the column by washing with 5 *N* nitric acid and lead by treating the resin with distilled water.

The distribution coefficients of some of the elements used in the separation experiments are shown in Table II. These coefficients were determined under exactly the same conditions as the column experiments, *i.e.* in 80% methanol and 20% 6 *N*

TABLE I

| *Amount of uranium used* µg | *Foreign ion used* | *Amount of foreign ion used* mg | *Uranium yield* µg |
|---|---|---|---|
| 100 | Fe(III) | 10 | 98 |
| 500 | Fe(III) | 10 | 510 |
| 100 | Co(II)[a] | 10 | 100 |
| 100 | Ni(II)[a] | 10 | 101 |
| 100 | Cu(II)[a] | 10 | 100 |
| 100 | Mg(II) | 10 | 100 |
| 100 | Ca(II) | 20 | 100 |
| 100 | Sr(II) | 3 | 99 |
| 100 | Ba(II) | 10 | 99 |
| 100 | Zn(II) | 10 | 102 |
| 100 | Cd(II) | 10 | 98 |
| 100 | Al(III) | 10 | 102 |
| 100 | La(III) | 10 | 96 |
| 100 | Ce(III) | 10 | 100 |
| 500 | Ce(III) | 10 | 508 |
| 100 | Nd(III) | 10 | 100 |
| 100 | Pr(III) | 10 | 105 |
| 100 | Yb(III) | 10 | 103 |
| 500 | La(III)<br>Ce(III)<br>Nd(III)<br>Pr(III)<br>Yb(III) | 5 each | 494 |
| 100 | Pb(II) | 5 | 92 |
| 100 | Ti(IV) | 0.5 | 100 |
| 100 | Zr(IV) | 5 | 96 |
| 100 | Hf(IV) | 1.6 | 98 |
| 100 | Bi(III) | 10 | 97 |
| 100 | V(V) | 3 | 99 |
| 100 | Cr(III) | 10 | 100 |
| 100 | Mo(VI) | 5 | 100 |
| 100 | Th(IV) | 25 | 98 |
| 500 | Th(IV) | 25 | 493 |
| 100 | Mn(II) | 10 | 100 |
| 100 | Na(I) | 30 | 104 |
| 100 | K(I) | 20 | 104 |
| 100 | Cs(I) | 2.5 | 104 |
| 100 | W(VI) | 0.2 | 100 |
| 100 | $F^-$ | 10 | 100 |
| 100 | $SO_4^{-2}$ | 5 | 98 |
| 100 | $NO_3^-$ | 10 | 100 |
| 100 | Sn(II) | 10 | 100 |
| 100 | $H_2PO_4^-$ | 10 | 100 |

[a] Uranium could be separated from a mixture of all the elements indicated in Table I irrespective of the amounts present, with the exception of cobalt, nickel and copper. If more than 1 mg of each of these 3 ions was present, their behaviour was strongly affected by the other cations present, so that they were strongly adsorbed however high the concentration of ascorbic acid in the mixture.

hydrochloric acid. The distribution coefficient $K_d$ is given by the following equation:

$$K_d = \frac{\mu\text{g element/g resin}}{\mu\text{g element/ml solution}}$$

This coefficient was determined as follows: 20 ml of methanol and 5 ml of 6 *N* hydrochloric acid containing the required element and 1 g of resin were transferred to a conical flask, which was stoppered and agitated on a shaking machine for 24 h. The resin was filtered off and the element was determined in the filtrate using a suitable analytical procedure.

TABLE II

| *Element* | *Distribution coefficient* $K_d$ |
|---|---|
| U(VI) | 867 |
| Th | 0.0 |
| Cu | 25[a] |
| Ni | 25[a] |
| Zr | 0.0 |
| Ti | 0.0 |
| Mo | 3.7 |

[a] In presence of 0.5 g of ascorbic acid

Table II shows that uranium has a rather high distribution coefficient whereas the other elements have only very small values under identical conditions; this illustrates the ease with which their separation from uranium can be achieved.

## ACKNOWLEDGEMENTS

This work was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under contract number 67/US. The generous support of these agencies is gratefully acknowledged.

## SUMMARY

A method for the separation of uranium(VI) from numerous elements by means of anion exchange is described; the negatively charged chloride complex of uranium is adsorbed on the strongly basic anion exchanger Dowex 1X8 (chloride form) from a solution containing 80% methanol and 20% 6 *N* hydrochloric acid. The uranium was determined by a polarographic method based on the catalytic nitrate wave of uranium.

## RÉSUMÉ

Une méthode est décrite pour la séparation de l'uranium(VI) d'avec de nombreux éléments, par échangeur d'anions. L'uranium est ensuite dosé par polarographie.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung von Uran-(VI) von zahlreichen anderen Elementen mit einem Ionenaustauscher und anschliessender polarographischer Bestimmung des Urans.

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# ON THE CONCENTRATION AND SEPARATION OF THE TRACE-ELEMENTS Fe, Cu, Zn, Mn, Pb, Mo and Co*

## III. PAPER CHROMATOGRAPHY

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(Received September 28th, 1960)

### INTRODUCTION

In applying paper chromatography for the concentration and separation of trace elements, the following points must be kept in mind:

(*1*) When the sample has to be ashed, the use of sulfuric acid must be avoided (or the sulfate ions must be removed, *e.g.* by anion exchange), because sulfuric acid would either cause destruction or (after neutralization) overloading of the paper.

(*2*) Concentration of a large aqueous volume into a small spot on the paper is required for satisfactory separations.

(*3*) Overloading of the paper by macro-constituents has to be watched. The maximum permissible amounts depend on the thickness of the paper and on the nature of both the sample and the solvent. From 0.5 to 10 mg can be handled per cm of Whatman No. 1 paper for instance.

(*4*) Separations are generally good, but a solvent separating all the 7 elements involved in the present study is hard to find. Thus either a split sample solution or two successive solvents are required.

(*5*) Combination with spectrography, densitometry and activation analysis is simple but for flame photometry, titrimetry, polarography and spectrophotometry elutions are required.

Special adaptations to "on the spot" analysis have been made for titration (LACOURT[1]), polarography (LANGER[2]), and several other electroanalytical methods including conductometry, oscillography, etc.[3-8].

As was demonstrated earlier[9,10], only a few radio-active reagents can be applied in paper chromatography. Most reagents adhere firmly to the paper and thus produce a high blank.

Analysis by exchange with radio-active metal ions has as yet not been carried out on filter paper.

In our experiments complexing agents were avoided (in either the paper or the solvent), as these agents will in general interfere with subsequent quantitative determinations. In order to keep the method as simple as possible, electrochromatography and chromatography on alumina columns were not considered.

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* Publication No. 128c of the Research Institute for Animal Husbandry "Schoonoord", Hoogt $10^{bis}$, Utrecht (The Netherlands).

## EXPERIMENTAL

*The chemicals* (see also part I and II) were all of reagent grade.

*All papers* contain traces of heavy metals (see part I). In Whatman No. 1 paper 0.1 to 1.0 μg per cm$^2$ are present. Iron occurs in small patches.

Washing of the paper with acidic methanol is the most effective method of purification[9]. Afterwards the paper must be neutralized and the water-content must be re-established.

*Procedure:* Cut strips of 2.5 or 3.0 × 50 cm and hang them in a jar. Rinse in the descending way, with 9:1 methanol–hydrochloric acid for 1 day, dry for 2 h and rinse for 1 day with 9:1 methanol–ammonia. Finally dry, rinse for 1 day with 95:5 methanol–water and dry in the atmosphere of the last solvent. These papers contain[9] about 0.03 μg of heavy metals per cm$^2$.

The *apparatus* consisted of ordinary chromatographic jars and sprays, a densitometer (see part I) and a home-made scanner for radio-activity.

In *ashing* the sample the use of sulfuric acid has to be restricted. Mixtures of nitric acid and hydrogen peroxide were unsatisfactory, even with the use of catalysts; perchloric acid was considered to be too dangerous for routine work. Dry ashing was chosen. A muffle furnace, with the inner dimensions: 30 × 17 × 9 cm, was used (Heraeus MR 170). To avoid losses by evaporation*, the temperature was kept between 400 and 450°.

*Procedure:* Weigh 0.1 g of dry material in a fairly new silica crucible (volume about 15 ml), moisten with 1 ml of 1 *N* sulfuric acid, cover with a lid and char for 1 h in a sand-bath at about 200°. Heat for 3 h in the muffle at 400 to 450°, cool, moisten with nitric acid and again heat for 3 h. Finally cool and dissolve in 1 *N* hydrochloric or nitric acid. When the sample contains much silica, treat with hydrofluoric acid in a platinum crucible.

*For the application of the sample to the paper,* no satisfactory method was found for the routine handling of large volumes of acid solutions[9]. Thus evaporation to a small volume and dipping of the paper in the residue were chosen. Evaporation was carried

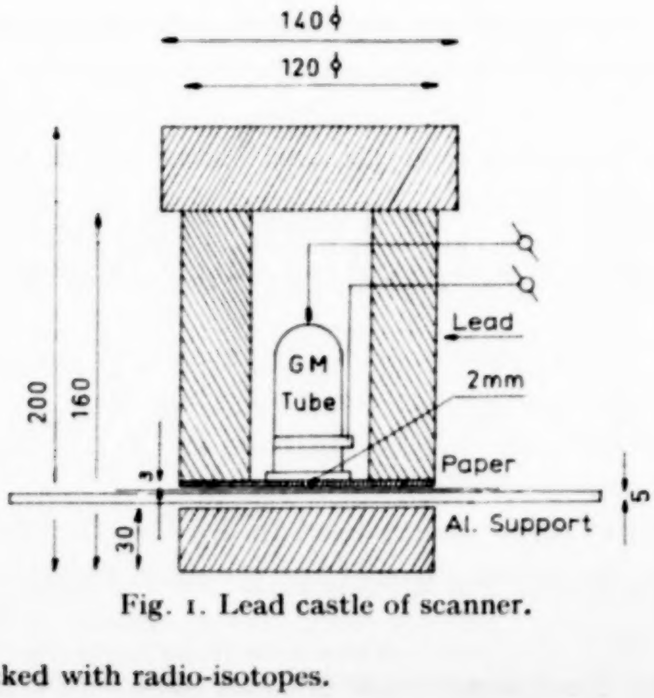

Fig. 1. Lead castle of scanner.

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* These losses were checked with radio-isotopes.

out in the silica crucible, following the method of THIERS *et al.*[11]; the final volume was 0.05 to 0.1 ml, the estimation of which is a matter of practice.

A washed paper strip was folded at 6 cm from one end and dipped into the residual solution until the spot was about 5 cm²; it was then dried in a clean atmosphere and dipped again until the crucible was empty (in all, 2 or 3 times). Experiments with radioisotopes indicated a 98% efficiency for this treatment.

*Results were again checked* with radio-isotopes* (see part I), but here the $\beta$-radiations were measured, with an end-window GM-tube (Fig. 1). $^{210}$Pb was measured after some $^{210}$Bi had grown in.

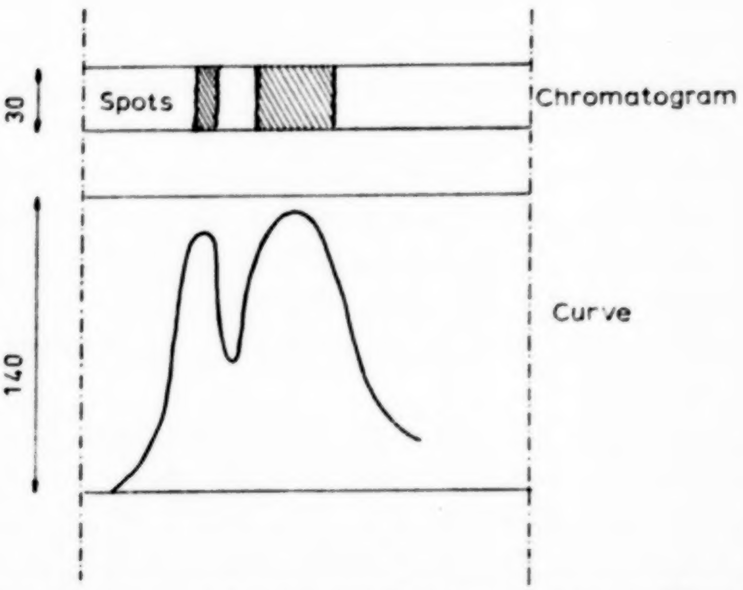

Fig. 2. Chromatogram and corresponding curve of the radioactive scan.

The peaks obtained with our scanning-apparatus and the GM-tube showed a distinct broadening as compared with the paper chromatogram (see Fig. 2). This broadening was probably due to secondary $\beta$'s from the accompanying $\gamma$-rays. Results with a scintillation counter were about the same, even when a 2 cm thick (2 mm wide) lead slit was applied. By comparison with simulated chromatograms, adequate conclusions could be drawn from the scanning curves.

## RESULTS

All results were obtained at 25 ± 1°. A solution of the ash of 0.1 g of dry cow liver in 0.1 ml of 1 *N* hydrochloric acid served as a sample. In general two techniques were employed:

(*A*) The spots were neither dried nor conditioned, and the chromatogram was run for 16 h, either in the ascending or in the descending way.

(*B*) The spots were dried for 1 h, conditioned for 16 h in the jar and run for 24 h in the ascending or in the descending way.

Fresh solvent mixtures were always used to develop the chromatograms, but the solvent(s) required for the atmosphere of the jar were added to it about 24 h before the experiment.

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* Copper was checked by densitometric scans (see part I).

Preliminary experiments and a survey of the literature indicated that the solvents ketone-hydrochloric acid and higher alcohol-hydrochloric acid were the most promising.

*Ketone-hydrochloric acid.* These solvents have been used by many authors[12-29]. From their results separations such as Mn — Co — Cu — Pb Fe Mo Zn — can be predicted.

In our experiments the atmosphere of the jar was made up from (*1*) acetone and (*2*) a saturated aqueous solution of ammonium nitrate.

The following solvents were applied (the composition is given in volume percentages):

(1 and 2) acetone–12 *N* hydrochloric acid: 92–8 and 94–6.
(3) acetone–8 *N* hydrochloric acid: 87–13.
(4, 5 and 6) acetone–6 *N* hydrochloric acid: 90–10, 95–5 and 98–2.
(7, 8 and 9) acetone–4 *N* hydrochloric acid: 80–30, 75–25 and 90–15.
(10) acetone–1 *N* hydrochloric acid: 90–11.
(11 and 12) acetone–butanol–12 *N* hydrochloric acid: 40–40–20 and 85–10–5.
(13 to 18) acetone–butanol–6 *N* hydrochloric acid: 75–10–15, 80–10–10, 75–20–5, 88–10–2 and 78–20–2.
(19) acetone–ethanol–isopropanol–6 *N* hydrochloric acid: 40–20–20–2.
(20) acetone–ethylacetate–6 *N* hydrochloric acid: 45–45–10.
(21) acetone–methylpropylketone–12 *N* hydrochloric acid: 50–42–8.
(22) acetone–methylisopropylketone–6 *N* hydrochloric acid: 50–42–3.
(23 and 24) methylisobutylketone–12 *N* hydrochloric acid: 92–8 and 90–6.
(25 and 26) methylethylketone–12 *N* hydrochloric acid: 92–8 and 94–6.
(27) methylethylketone–7 *N* hydrochloric acid: 75–25.

The most satisfactory separations were obtained with ascending chromatography as follows (the first figure designates the solvent and A or B indicates which technique was used) (see above):

9-A: Mn 40-Co 57-Pb 73-Cu 85-M 98,

13-B: Pb 5 to 20-Mn 35-Co 65-Cu 82-M 98, and

16-A: Mn 18-Co 38-Pb 59-Cu 66-M 98, in which the mean $R_F$-values of the elements are given and M stands for the mixture Fe + Zn + Mo.

Results with unwashed papers were slightly better than those with acid-washed ones. The most reproducible results were obtained with solvent 16. This solvent does not provide a very good separation of lead and copper. However, specific determinations on the paper are available for both elements; in addition a second separation of lead and copper can be obtained as described below.

*Higher alcohol-hydrochloric acid.* These solvents have also been applied by many authors[12,13,14,22,28-40]. From their results[11,13,14,20,26-39] separations such as Mn—Cu—Co—Pb—Fe—Mo—Zn can be predicted.

In our experiments the alcohol was either saturated or mixed with the hydrochloric acid. In the first case the atmosphere of the jar was made up from the two phases; in the second case the solvent alone was used for this purpose. Saturation of the alcohol with the acid was carried out at 25 ± 1°, then 10% of alcohol was added, to prevent the separation of the solvent in two layers.

The following solvents were applied:

(1 to 6) butanol saturated with 1, 2, 2.5, 3, 3.5 and 4 *N* hydrochloric acid respectively.
(7) butanol–3.8 *N* hydrochloric acid: 15–4.
(8 and 9) butanol–5 *N* hydrochloric acid: 10–5 and 9–1.
(10 and 11) butanol–12 *N* hydrochloric acid: 80–20 and 95–5.

(12) butanol saturated with water–12 *N* hydrochloric acid: 92–8.
(13) butanol–12 *N* hydrochloric acid – conc. sulfuric acid: 60–12–1.
(14) butanol–12 *N* hydrochloric acid – 3% hydrogen peroxide: 100–4–20.
(15 and 16) butanol saturated with 1 *N* and 2 *N* hydrobromic acid.
(17) butanol saturated with a 1:1 mixture of 2 *N* hydrochloric and 2 *N* nitric acid.
(18 and 19) butanol–*n*-pentanol: 1–1, saturated with 2 *N* and 3 *N* hydrochloric acid.
(20) butanol–isopropanol: 1–1, mixed with 5 *N* hydrochloric acid: 90–10.
(21 and 22) *n*-pentanol saturated with 2 *N* and 3 *N* hydrochloric acid.
(23) *n*-pentanol–12 *N* hydrochloric acid: 80–20.

The most satisfactory separation obtained was with solvent 3 or 4 and descending chromatography and with either of the techniques A or B: M′ 8 – Pb 22 – Fe 41 – Mo 67 – Zn 88 in which again the mean $R_F$-values are given, and M′ stands for the mixture Cu + Co + Mn. Results with washed and unwashed papers were similar. In contrast to WELLS[15] no influence of the drying method (hot or cold) on the $R_F$-value of iron was observed.

As all the solvents selected proved to be unsatisfactory when used singly or in mixtures of 2 solvents, a split sample technique was adopted.

## PROCEDURE

Dissolve the sample or its ash (see p. 227) in a minimum amount of hydrochloric or/and nitric acid; add radioactive tracers and evaporate to a small volume. Dip an acid-washed paper in the residue (see p. 228). Without further drying or conditioning,

TABLE I

COMPARISON OF PART I, II AND III

| | *Ion exchange* | *Solvent extraction* | *Paper chromatography* |
|---|---|---|---|
| *System chosen* | *Cation exchange, with selective elution by acetone–HCl–$H_2O$ mixtures* | *Acetylacetone, combined with diethyldithiocarbamate* | *Split sample, with the solvents: acetone–butanol–HCl and butanol–HCl* |
| Separation[a] obtained | Mo–Fe[b]–Co[b]<br>Cu Mn<br>Zn<br>Pb | Mo–Fe–Mn–Zn–Pb–Co<br>Cu | Mn–Co–Pb–Cu–Fe<br>Mo<br>Zn<br>and<br>Cu–Pb–Fe–Mo–Zn<br>Co<br>Mn |
| Ashing | Wet or dry | Wet or dry | Dry |
| Concentration of traces | Good | Good | Reasonable |
| Combination with quant. techniques | Excellent | Excellent: flame photometry, spectrography, activation analysis<br>Partly: spectrophotometry, radiometric analysis<br>Not: polarography | Excellent: spectrography, densitometry, activation analysis[c], some radioactive reagents<br>Not: flame photometry, spectrophotometry, polarography, most radiometric techniques |
| Maximum sample (in g of dry cow liver) | 3 (per 4 ml column) | 1 | 0.1 per 2.5 cm width Whatman No. 1 paper<br>0.3 idem No. 3 MM |

[a] Required separations: Fe from Mn, Mo, Co; Cu from Co; Mn from Zn.
[b] Further separation is possible by anion exchange from 9 *N* HCl.
[c] Here activation can be carried out after the separation.

run the sample at 25° for about 16 h in the ascending way with the fresh solvent mentioned in the section on ketone–hydrochloric acid. The jar should be saturated with acetone and with a saturated solution of ammonium nitrate for 24 h before the experiment. Repeat this procedure with another part of the sample, using the solvent 3 or 4 mentioned in the section on higher alcohols-hydrochloric acid, this time chromatographing in the descending way. Dry both chromatograms and control the separation as described on p. 228.

## CONCLUSIONS ON PART III. COMPARISON WITH PART I AND II

In conclusion, when a split sample is used, satisfactory results can be obtained with paper chromatography. As indicated in the introduction, the sample should be dry-ashed. Concentration of the trace elements is difficult. The size of the sample is restricted. Finally, combination with many quantitative techniques cannot easily be achieved. In general, paper chromatography does not offer many advantages over the separation techniques described in parts I and II. Its value depends of course on the problem to be handled. A comparison of the three techniques is given in Table I.

For general work, ion exchange is to be preferred, as combinations with quantitative techniques are easily made, while the size of the sample is in principle unlimited. When rapidity is of great value, solvent extraction is advantageous.

Paper chromatography can elegantly be combined with activation analysis carried out on the prepared chromatogram.

## ACKNOWLEDGEMENT

The author's thanks are due to Miss J. H. F. F. BROEKMAN for valuable technical assistance.

## SUMMARY

Paper chromatographic separations are described by which the minor constituents of biological ashes are separated either into: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; or into: Cu, Mn, Co – Pb – Fe – Mo – Zn.

## RÉSUMÉ

La chromatographie sur papier est utilisée pour la séparation des éléments oligodynamiques des cendres biologiqnes. Les séparations obtenues sont: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn, et Cu, Mn, Co – Pb – Fe – Mo – Zn.

## ZUSAMMENFASSUNG

Papierchromatografische Trennungen der Bestandteilen von biologischen Aschen werden beschrieben. Die Spurenelementen dieser Aschen werden entweder getrennt in die Gruppen: (Pb) – Mn – Co – (Pb) – Cu – Fe, Mo, Zn; oder in die Gruppen: Cu, Mn, Co – Pb – Fe – Mo – Zn.

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# ABSORPTIOMETRIC DETERMINATION OF SULFATE IN WATERS

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(Received January 2nd, 1961)

## INTRODUCTION

The dehydrating action of concentrated sulfuric acid on some organic compounds, *e.g.* glucose, saccharose and cellulose, may serve as a basis for the identification as well as for the determination of free sulfuric acid. FEIGL[1] describes a test for small quantities of sulfuric acid, that consists of the evaporation of the solution in presence of glucose, and heating of the residue at 120°; the dehydrating action of the concentrated sulfuric acid causes charring of the glucose. MEDITSCH[2] has shown the possibility of semiquantitative determination of traces of sulfuric acid by comparison of the spot obtained when filter paper impregnated with the solution is heated at 170° for 10 min, with standard spots.

The authors have developed a method for the absorptiometric determination of sulfate in waters, based on the dehydrating action of sulfuric acid on saccharose. The sulfate is converted to free sulfuric acid by means of a cation exchange resin, and the solution is evaporated to dryness in presence of saccharose and then the residue is heated at 85° for 60 min. The residue has a bottle-green colour and when dissolved in water forms a brown-yellowish solution which is suitable for absorptiometric determination.

All the strong mineral acids (hydrochloric acid, phosphoric acid, nitric acid, perchloric acid) react with the saccharose in the same way as the sulfuric acid. The stronger organic acids, such as trichloroacetic acid ($\mathrm{p}K = 0.89$) and oxalic acid ($\mathrm{p}K_1 = 1.19$) react similarly. Weak reactions occur with dichloroacetic acid ($\mathrm{p}K = 1.30$), monochloroacetic acid ($\mathrm{p}K = 2.82$), tartaric acid ($\mathrm{p}K_1 = 3.02$), citric acid ($\mathrm{p}K_1 = 3.06$) and sulfanilic acid ($\mathrm{p}K = 3.19$). The weaker organic acids, such as formic acid ($\mathrm{p}K = 3.75$) and acetic acid ($\mathrm{p}K = 4.75$) that are volatile, do not react. Lactic acid ($\mathrm{p}K = 3.85$) reacts very weakly.

## EXPERIMENTAL

### *Apparatus*

(*a*) Klett-Summerson Photoelectric Colorimeter. Standardized test tubes (12.5 mm internal diameter).

(*b*) Ion exchange column, as described by TOMPKINS *et al.*[3].

### *Preliminary tests*

If a solution containing small quantities of sulfuric acid and saccharose is evaporated to dryness, and the residue is then heated for some time, the saccharose is submitted to a dehydrating process, the extent of which increases as the ratio of sulfuric acid to saccharose increases and as the temperature and time of heating are increased. Incomplete dehydration leaves a residue which dissolves in water to form a sufficiently stable solution. After a certain degree, the dehydration leads to almost total charring of saccharose and most of the residue does not dissolve.

Fig. 1 shows the absorption curve of a solution obtained by the following treatment: (*a*) evaporation to dryness of a mixture of 10.00 ml of sulfuric acid containing about 0.25 mg of sulfate and 5.00 ml of 0.2% saccharose solution on steam bath; (*b*) heating of the residue at 85° for 60 min; (*c*) dissolution of the residue in 10.00 ml of water. The absorption curve shows a maximum at about 420 m$\mu$.

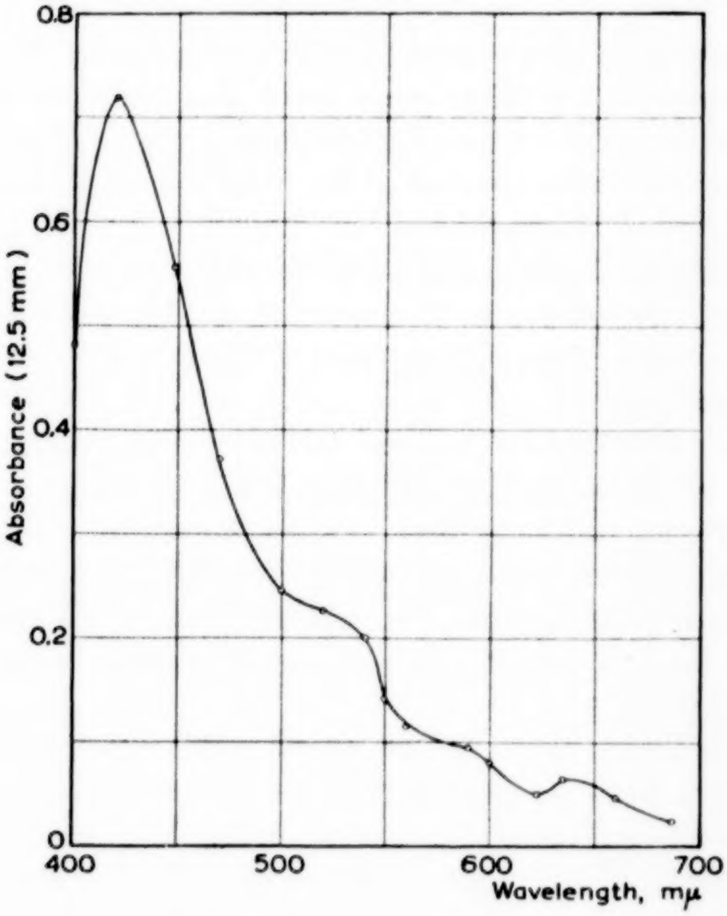

Fig. 1. Absorption curve.

In order to study the exact effects of temperature and heating time for the development of a proper analytical method, different quantities of sulfuric acid at a temperature of 85, 90 or 95°, with a heating time of 30 or 60 min were examined. Fig. 2 shows six absorbance–concentration curves that correspond to the following conditions: (*a*) heating at 85° for 30 min (curve I); (*b*) heating at 85° for 60 min (curve III); (*c*) heating at 90° for 30 min (curve II); (*d*) heating for 60 min at 90° (curve V); (*e*) heating at 95° for 30 min (curve IV); (*f*) heating at 95° for 60 min (curve VI).

A comparison of the six curves shows that the effects of small variations in temperature and heating time are large, hence it would seem necessary to control these factors rigidly. A more practical solution, however, is to trace the reference curve each time; this is simple because only two points are required for the straight line reference graph. The simultaneous treatment of the standard and sample solutions compensates for any variations in the temperature and heating time provided that a drying oven of homogeneous internal temperature is available. The changes in the absorbance with the sulfuric acid concentration, the ranges of sulfuric acid which could be determined, and a comparison of the regions for absorptiometric measurements, all indicated that the conditions of curve III, *i.e.* heating at 85° for 60 min

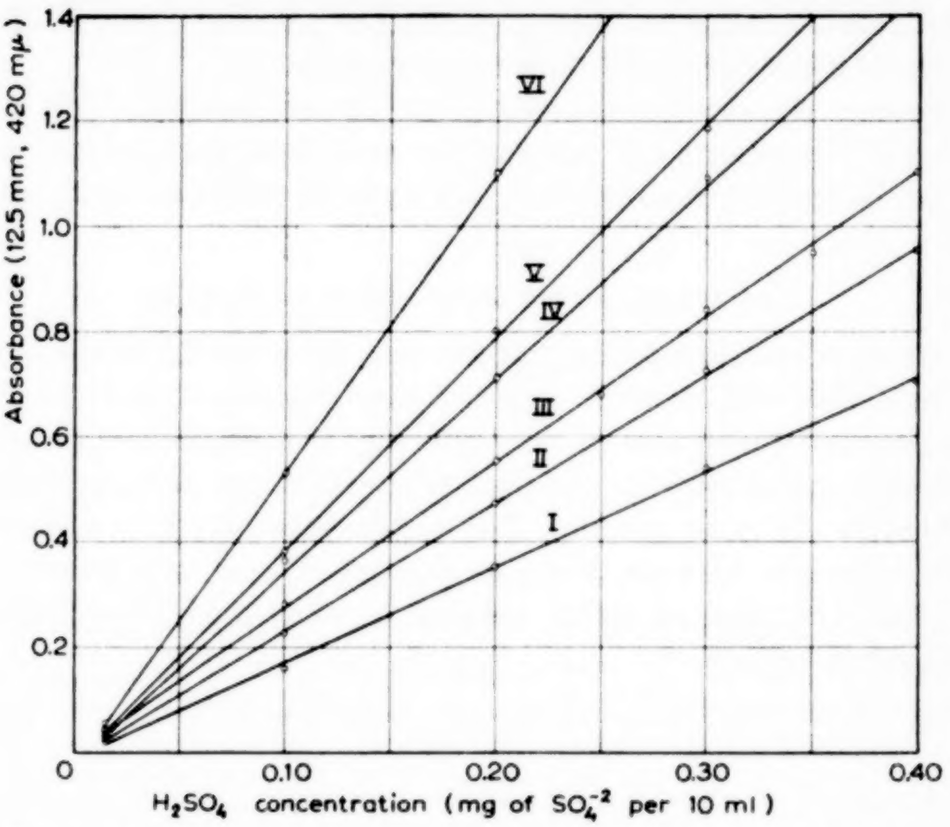

Fig. 2. Absorbance–concentration curves for different conditions.

TABLE I

DETERMINATION OF DIFFERENT AMOUNTS OF SULFURIC ACID

| *Amount taken (mg of $SO_4^{-2}$)* | *Amount found (mg of $SO_4^{-2}$)* | *Relative error (%)* |
|---|---|---|
| 0.050 | 0.048 | −4.0 |
| | 0.051 | +2.0 |
| | 0.052 | +4.0 |
| | 0.050 | — |
| | 0.049 | −2.0 |
| 0.200 | 0.201 | +0.5 |
| | 0.203 | +1.5 |
| | 0.197 | −1.5 |
| | 0.201 | +0.5 |
| | 0.198 | −1.0 |
| 0.300 | 0.297 | −1.0 |
| | 0.305 | +1.7 |
| | 0.297 | −1.0 |
| | 0.301 | +0.3 |
| | 0.303 | +1.0 |

were most suitable for an analytical procedure. Under such conditions it is possible to work with up to 0.40 mg (40 p.p.m.) of sulfate without danger of formation of an insoluble residue. The resultant coloured solutions are relatively stable. The decrease in the absorbance with time is more noticeable with the more concentrated solutions; the decrease after 1 h is only 0.002 units for solutions containing 0.05 mg (5 p.p.m.) of sulfate but reaches 0.010 units for 0.30 mg (30 p.p.m.) of sulfate. It is preferable to measure the absorbance of the solution immediately.

Table I presents the results obtained in the determination of different quantities of sulfuric acid. The results are satisfactory and show the possibility of using the reaction of saccharose with sulfuric acid as a basis for the determination of sulfate.

## DETERMINATION OF SULFATE IN WATERS

In the conversion of sulfate into free sulfuric acid, with the aid of the cation exchange resin, the carbonate and chloride ions are also converted into the respective free acids. As hydrochloric acid acts in the same way as sulfuric acid on saccharose, it is necessary to separate chloride by precipitation with silver acetate before the solution is passed through the resin column. The appearance of acetic acid in the solution does not cause trouble, because it is a weak organic acid which does not react with saccharose. The filtration of silver chloride is simplified by addition of a small quantity of barium sulfate.

### *Procedure*

Measure 25.00 ml of water into a beaker and add about 0.2 g of barium sulfate and 5 ml of 0.01 *M* silver acetate solution. Boil for 3 min and let cool. Transfer to a 50-ml volumetric flask and dilute to the mark. Filter through filter paper (S & S, no. 589, red ribbon) directly into the bulb of the exchange column loaded with Amberlite IR-120. Let the solution flow through at a rate of 0.01–0.05 ml/ml of resin/min. Reject the first 20 ml, and from the rest of the cation-free solution measure 20.00 ml (this corresponds to 10.00 ml of the original sample) into a porcelain dish of diameter 7.5 cm. Add 5.00 ml of 0.2% saccharose solution and evaporate on a steam bath until exactly dry. As soon as evaporation is complete, transfer the dish to a drying oven at 85°, and leave it there for 60 min. Let it cool and dissolve the residue in 10.00 ml of water. Transfer the solution to the standardized test tube and measure the absorbance at 420 m$\mu$. Simultaneously, treat as above: (*a*) 10.00 ml of sulfuric acid solution containing 10.0 p.p.m. of sulfate, and (*b*) 10.00 ml of sulfuric acid solution containing 30.0 p.p.m. of sulfate, in order to obtain the standard curve. The result in p.p.m. is expressed by

$$R = 10 + \frac{20d}{d'}$$

where $d$ and $d'$ are, respectively, the differences of absorbance of the sample solution and the more concentrated standard (30 p.p.m.) with relation to the absorbance of the lower standard (10 p.p.m.).

This process was applied to the determination of sulfate in two water samples of the Pôrto Alegre city public supply, containing, respectively, 14.1 and 21.2 p.p.m.

of sulfate. Each water sample was submitted to five determinations and the results found are shown in Table II.

TABLE II

THE DETERMINATION OF SULFATE IN WATERS

| *Sample* | *Result (p.p.m. $SO_4^{-2}$)* | *Relative error (%)* |
|---|---|---|
| No. 1 | | |
| (14.1 p.p.m. $SO_4^{-2}$) | 13.7 | —2.8 |
| | 14.2 | +0.7 |
| | 13.7 | —2.8 |
| | 14.5 | +2.8 |
| | 14.4 | +2.1 |
| No. 2 | | |
| (21.2 p.p.m. $SO_4^{-2}$) | 21.6 | +1.9 |
| | 21.6 | +1.9 |
| | 21.4 | +1.0 |
| | 20.8 | —1.9 |
| | 20.9 | —1.4 |

## CONCLUSION

The results obtained show that the method of absorptiometric determination of sulfate in waters, based on the dehydrating action of sulfuric acid on saccharose, leads to satisfactory results and that the analytical process is of easy and rapid execution.

## SUMMARY

An absorptiometric method is proposed for sulfate determination, based on the colour produced by heating sulfuric acid with saccharose at 85° for 60 min. The method was applied to the determination of sulfate in treated waters; chloride was removed by precipitation with silver acetate, and sulfate was converted to sulfuric acid with a cation exchange resin column.

## RÉSUMÉ

Une méthode absorptiométrique est proposée pour le dosage du sulfate dans les eaux. Elle est basée sur la coloration obtenue par chauffage de l'acide sulfurique en présence de saccharose. Le sulfate est transformé en acide sulfurique par échangeur de cations.

## ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Sulfat in Wasser. Sie beruht auf der Ueberführung des Sulfates in Schwefelsäure mit einem Austauscherharz und Messung der Färbung, die bei der Einwirkung der Schwefeisäure auf Sacchararose entsteht.

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# THE DETERMINATION OF MAGNESIUM WITH TITAN YELLOW

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(Received January 9th, 1961)

## INTRODUCTION

Since KOLTHOFF[1] introduced titan yellow as a reagent for the determination of magnesium, several investigators have tested this reagent.

In its simplest form, in which titan yellow and sodium hydroxide are added to the solution to be analysed, the method tends to give variable results owing to the low uniformity and instability of the magnesium hydroxide colloid; moreover, the colouring depends on an adsorption reaction, which itself depends on several factors, and the colour of the titan yellow is liable to fade. These difficulties can be partly eliminated by adding a protective colloid to increase the stability of the colloidal solution. To prevent fading the addition of a stabilizer has occasionally been recommended. In spite of these improvements, however, the reaction remained uncertain, especially in the presence of other ions.

In 1950 a method for the determination of magnesium in soils with titan yellow was published by the author in co-operation with LEHR[2] and in this several improvements were introduced. Its reproducibility sometimes proved to be unsatisfactory, however, and the influence of several factors has therefore been studied. The results of these investigations are given below.

## INVESTIGATION OF FACTORS

In our method 5 ml of 5% hydroxylamine hydrochloride, 10 ml of 1% carbocel and 10 ml of 0.1% titan yellow solution are added to 50 ml of the test solution which should be shaken gently and be free from interfering ions. 10 ml of sodium hydroxide solution are then added, while shaking steadily. The intensity of the colour produced is measured at 530 m$\mu$ against a blank obtained in the same way but starting from 50 ml of distilled water.

### *Titan yellow*

In the course of time titan yellow has proved to be a rather complicated reagent and its name has become subject to discussion. ABRAHAMCZIK[3] and BEČKA[4] mentioned that titan yellow is marketed under different names, *e.g.*, titan yellow, thiazole yellow, Clayton yellow and acidin yellow. This is confirmed by HUNTER[5] who also indicates that there are differences between products of different origin and even between preparations of the same origin. According to MIKKELSEN AND TOTH[6] thiazole yellow is the most suitable reagent. In our experience, however, there are no specific differences between products of different name.

Differences in the colour intensity of the reagents which were at our disposal were striking. The magnitude of these differences is shown in the last column of Table I, where the figures represent the percentages of absorption of 0.05% aqueous solutions of the dyes measured against water as a blank at 530 mμ in 18-mm tubes. The colour intensity of the Grübler, Brocades and Merck products do not differ much, except for one preparation of Brocades. The B.D.H. preparations are stronger coloured.

The sensitivity of each dye was determined by measuring the colour intensity produced with 0.25 mg of magnesium according to the method mentioned earlier, against a blank at 530 mμ.

TABLE I

COLOUR AND SENSITIVITY OF DIFFERENT TITAN YELLOW PRODUCTS

| *Name of dye* | *Origin* | | *Sensitivity (% absorption)* | *Colour of dye (% absorption)* |
|---|---|---|---|---|
| Titan yellow | Grübler | 1 | 56.0 | 67.0 |
| | | 2 | 57.5 | 65.3 |
| | Brocades | 1 | 59.0 | 65.3 |
| | | 2 | 61.0 | 87.2 |
| | | 3 | 56.0 | 67.0 |
| | | 4 | 58.0 | 66.2 |
| | Merck | 1 | 59.0 | 67.8 |
| | | 2 | 58.5 | 67.0 |
| | | 3 | 54.0 | 68.7 |
| | B.D.H. | 1 | 55.0 | 86.7 |
| | | 2 | 59.0 | 84.5 |
| | Kodak | | 45.0 | 82.8 |
| Thiazole yellow | Geigy | 1 | 45.0 | 79.3 |
| | | 2 | 45.0 | 82.6 |
| | General Aniline Works | 1 | 55.5 | 92.5 |
| | | 2 | 52.0 | 93.2 |
| | "Kolen Cie" | | 57.0 | 90.5 |
| Clayton yellow | Hartmann | | 55.5 | 83.7 |
| | Unknown | | 55.0 | 87.8 |

From the figures it can be seen that the products differ in sensitivity although, as the identical trend of the absorption curves show (Fig. 1), the compound is the same in each case. There is no relation between the colour of the dye and its sensitivity.

Since the different products are identical we shall therefore always speak of titan yellow.

### *Stability of the solution*

There are several different opinions on the stability of aqueous titan yellow solutions. PIETERS *et al.*[7] prepare their solution daily, while KUNKEL *et al.*[8] prepare it every ten days, and PEECH[9] considers it stable for two months. Under our conditions, where the solutions were kept in brown flasks in the dark, a 0.1% solution proved to be stable for at least three months.

TABLE II

AMOUNTS OF TITAN YELLOW USED IN RELATION TO MAGNESIUM CONCENTRATION IN DIFFERENT PROCEDURES

| *Author* | *Reference* | *mg Mg* | *mg titan yellow* | *Titan yellow per mg Mg* |
|---|---|---|---|---|
| Urbach and Baril | 10 | 0.033 | 0.1 | 3.0 |
| Glemser and Dautzenberg | 11 | 0.050 | 0.4 | 8.0 |
| Pieters *et al.* | 7 | 0.050 | 2.5 | 50.0 |
| Urbach and Baril | 10 | 0.071 | 1.0 | 14.1 |
| Urbach and Baril | 10 | 0.100 | 1.5 | 15.0 |
| Urbach and Baril | 10 | 0.122 | 2.0 | 16.4 |
| Drosdorff and Nearpass | 12 | 0.15 | 1.0 | 6.7 |
| Sandell | 13 | 0.15 | 0.5 | 3.3 |
| Deys and Hekman | 14 | 0.18 | 2.0 | 11.1 |
| Sterges and McIntire | 15 | 0.20 | 0.5 | 2.5 |
| Glemser and Dautzenberg | 11 | 0.24 | 2.0 | 8.3 |
| Cottenie | 16 | 0.24 | 1.0 | 4.2 |
| Kawe Andersson | 17 | 0.30 | 1.0 | 3.3 |
| Gillam | 18 | 0.30 | 0.45 | 1.5 |
| Mikkelsen *et al.* | 19 | 0.30 | 0.50 | 1.7 |
| Ludwig and Johnson | 20 | 1.1 | 5.0 | 4.5 |
| Glemser and Dautzenberg | 11 | 1.6 | 14.0 | 8.7 |

### *Required amount of titan yellow*

As the titan yellow is adsorbed by the magnesium hydroxide particles, it is likely that for a given amount of magnesium a minimum quantity of titan yellow is required. Pieters *et al.*[7] determined the amount of titan yellow necessary and expressed it by the equation: $a = 2x + 2.4$ in which $x$ is the amount of magnesium in mg and $a$ the amount of titan yellow in mg. Urbach and Baril[10] found a close relationship between the amount of titan yellow required and the magnesium concentration. From different procedures described in the literature we calculated the amounts of titan yellow used for given quantities of magnesium (Table II).

It will be seen that the amount of titan yellow per mg of magnesium varies considerably. According to Pieters *et al.*[7] the quantity required for 0.1–0.3 mg of magnesium is 2.6–3.0 mg, which is larger than that generally used. Urbach and Baril[10] also use large quantities of titan yellow. In general it would seem that the quantities of titan yellow are on the low side and it is possible that under such conditions the results would show a greater variability as there is an equilibrium between the amount of titan yellow adsorbed and in solution. Moreover, the differences in the amounts of titan yellow required may be caused by the circumstances under which the magnesium hydroxide has been formed. The size of the particles determines the amount of titan yellow adsorbed.

Bussmann[21] advises against the use of too large an excess of the reagent but the amount he applies — 10 mg per mg of magnesium — is higher than that generally used. It is our experience that with an ample quantity of reagent better and more reproducible results are obtained. We therefore recommend the use of 10 mg of titan yellow for quantities up to 0.4 mg of magnesium, giving a ratio of 25.

### *Influence of sodium hydroxide*

According to Kolthoff[1,22] the colour of the titan yellow solution changes from yellow to brown to yellow again as the concentration of sodium hydroxide increases. The influence of the hydroxide on the colour intensity was determined by us by measuring the absorption of solutions obtained by adding 10 ml of 0.1% titan yellow and 10 ml of sodium hydroxide solutions of increasing concentrations to 65 ml of water. The intensities were measured at different wavelengths against a blank obtained by adding 10 ml of 0.1% titan yellow solution to 75 ml of water. The absorption curves showed the same trend for all the tested concentrations. There was only an increase in intensity from 2 $N$ to 4 $N$ sodium hydroxide. With further increase in concentration the intensity decreased. The influence of the sodium hydroxide, however, is not of decisive significance for the choice of the alkali concentration.

### *Protective colloid*

Many protective colloids have been used, for example, gum ghatti, gum arabic, gum acacia, dextrin, gelatine, agar agar, starch, ethyloxyethylcellulose and polyvinyl alcohol. Most of these are not very suitable as they are difficult to purify and the solutions must be prepared daily. Moreover, there are often differences in quality, even when the products are of the same origin. Compared with some other colloids, cellulose derivatives and polyvinyl alcohol are more stable in solution and have a greater stabilizing effect.

In our procedure the sodium salt of carboxymethylcellulose ("Nymcel") is used. The solution is very stable, especially under acid conditions. In a number of procedures protective colloids are not used[8,9,13,18,23–26].

### *Colour stabilizer*

To prevent fading of the colour a solution of hydroxylamine hydrochloride is often added. According to MIKKELSEN AND TOTH[6] this stabilizer also prevents oxidation, while PEECH AND ENGLISH[27] noted an elimination of the interference of manganese and iron. KUNKEL *et al.*[8] point out that the shape of the standard curve depends on the ratio of the amounts of titan yellow and hydroxylamine hydrochloride used. DEYS AND HEKMAN[14] did not find this stabilizer suitable and they recommend ferric ions as a stabilizer. We found that the colour faded rapidly if no stabilizer was added. With hydroxylamine hydrochloride satisfactory results were obtained and the colour proved to be constant for at least 45 min.

### *Influence of sodium hydroxide on the reaction*

After adding the sodium hydroxide solution magnesium hydroxide is formed. It is likely that reproducible results are only obtained when the magnesium hydroxide particles are all of the same size. Variations in the standard curve may be due to differences in size of the particles, a reason which is also put forward by SCHACHTSCHABEL AND ISERMEYER[28]. On the other hand the amount of sodium hydroxide must be sufficient to ensure complete reaction and, considered in this light, it is striking that the amounts of sodium hydroxide used in the different procedures vary considerably. The influence of the sodium hydroxide is very important and some aspects of this were studied.

(*a*) *The shape of the curve.* The influence of hydroxide concentration was investigated by dissolving increasing amounts of magnesium in 50 ml of water (0–0.4 mg of Mg).

To these solutions 5 ml of 5% hydroxylamine hydrochloride, 10 ml of 1% Nymcel and 10 ml of 0.1% titan yellow solution were added. Finally 10 ml of sodium hydroxide solution of increasing concentration were added, *viz.* 2, 4, 6 and 8 *N*. The shape of the curve proved to be dependent on the concentration, as shown in Fig. 2a.

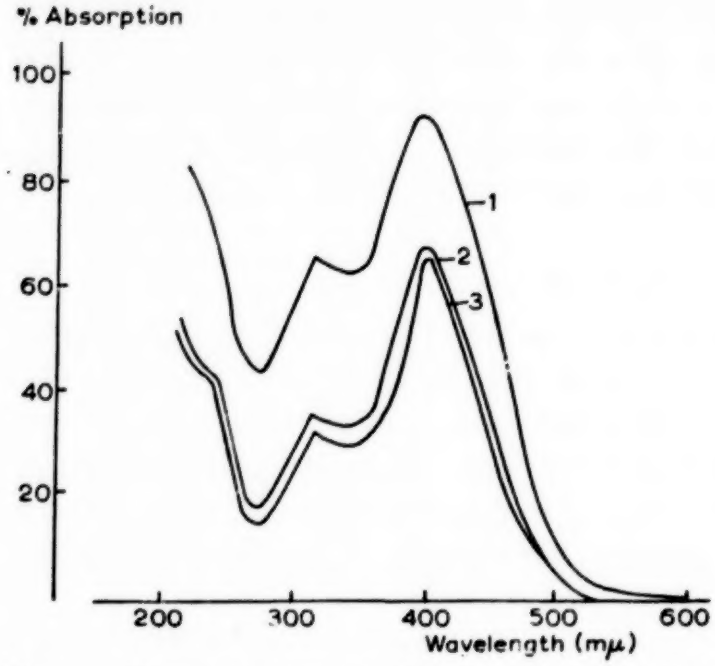

Fig. 1. Absorption curves for 3 products of titan yellow. (*1*) thiazole yellow (General Aniline Works, see Table I); (*2*) titan yellow (Merck, No. 3, see Table I); (*3*) titan-yellow (unknown).

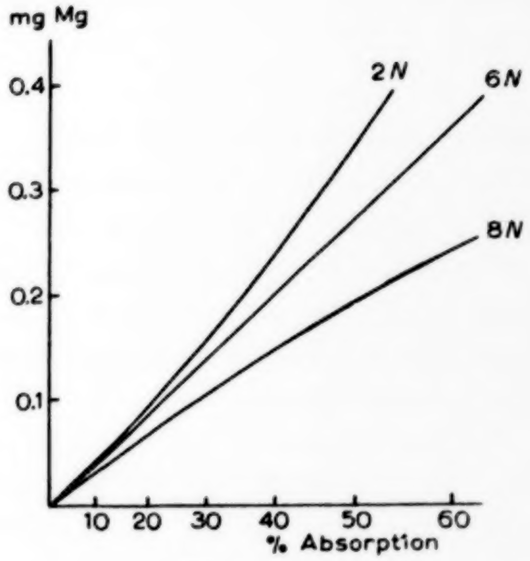

Fig. 2a.

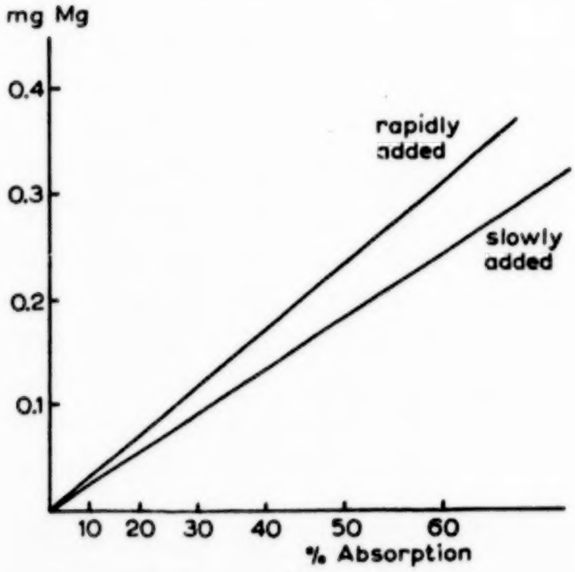

Fig. 2b.

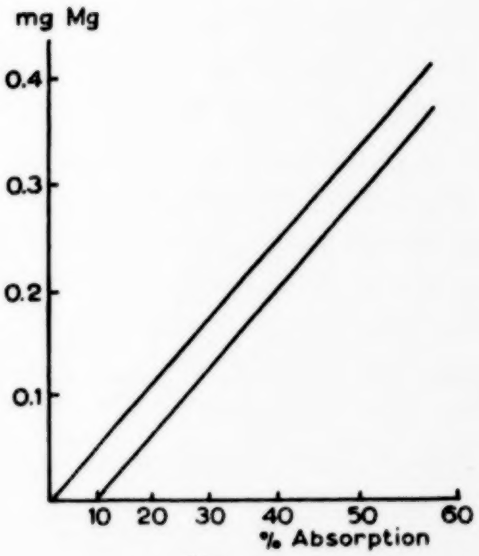

Fig. 2c.

Fig. 2a. Influence of NaOH on shape of curve; 2b. Influence of NaOH on slope of curve; 2c. Influence of NaOH on position of curve.

Using Merck's titan yellow a straight standard curve was obtained with 6 *N* hydroxide when plotted on semi-log paper. At lower and higher concentrations the shape of the curve was different. With other titan yellow products a straight standard curve can also be obtained, but it appears that each product requires a specific amount of hydroxide. For instance, the titan yellow of Grübler and that of Baird and Tatlock required 7 and 8 *N* alkali respectively to give a straight line. The reproducibility is improved by taking that amount of alkali with which a straight standard curve is obtained.

(*b*) *The slope of the curve.* The slope of the standard curve was found to be affected by the use of different pipettes, as this caused differences in the velocity with which the alkali was added. In Fig. 2b the influence of velocity is shown. When the hydroxide is added slowly, the colour intensity increases. The standard curve remains a straight line, but the slope of the curve differs at different velocities. The time in which the hydroxide is added should be at least 20 sec. Small variations in time do not result in significant differences.

(*c*) *The position of the curve.* Often the standard curve does not pass the origin, but intercepts the X axis, as shown in Fig. 2c, still showing the same slope so that the curves obtained are parallel. This was also observed by Cottenie[16]. The parallel shifting of the curve is evidently induced by the fact that the colour intensity of the blank solution also depends on the rate at which the hydroxide is added. The variations in colour intensity of the blanks are more pronounced when the hydroxide is added rapidly. The greater the amount of time for the addition, the smaller are the variations of the blank; when enough time is taken the standard curve always passes the origin.

(*d*) *Timing of measurement of curve.* Some investigators measure the colour intensity immediately after addition of the sodium hydroxide[13,15,18,25,29] while others do so 5–10 min[11,12,16,17,30–32] or even 10–40 min[7,8,14,19,23,26,33,34] afterwards. From these figures it may be concluded that the stability of the colour differs considerably in the different procedures. With our method, using Merck's titan yellow, the colour reaches its maximum after 20–30 min and remains constant for at least 45 min. The increase in colour intensity in relation to the time of standing after the addition of the hydroxide is not due to an increase of the colour produced by magnesium, however, but to a decrease of the colour intensity of the blank.

### *Mixing the reagents*

The addition of the reagents is rather time-consuming. We tried to save time by mixing the solutions of the protective colloid, the stabilizer and the titan yellow in the ratio of 1 : 2 : 2 beforehand. This mixed solution proved to be stable for at least a month when kept in the dark. It should be prepared two or three days before use as there is an increase in sensitivity showing a maximum after some days' standing. This method has the advantage that the stability of the Nymcel is higher because the solution has an acid reaction.

### *Influence of light and temperature*

The influence of light and temperature is uncertain. The colour fades rapidly when exposed to direct sunlight and may fade in diffuse daylight. To prevent any influence we produce the colours in flasks which are painted black. Small fluctuations in room temperature have no effect.

### *Interfering ions*

We shall only discuss the influence of those interfering ions which are normally present in soil and plant material.

(*a*) *Calcium.* Calcium has generally been found to give an increase in colour intensity[3,4,7,9,17,19,20,22,31] but Okamoto and Thomas[35] report a decrease. Urbach and Baril[10] only found an influence on the blank. Most of the titan yellow products tested by us showed an increase in colour intensity but some showed a decrease and one showed no influence at all. With Merck's titan yellow there was no effect on the blank, but a clear effect on the colour produced by magnesium. The character of the effect of calcium thus depends on the titan yellow used. There are many methods of eliminating the influence of calcium, for example:

(*1*) compensating solution[11,16,17,20,26,34]. In this case so much calcium is added that there is a maximum effect. Fluctuations in calcium concentration then have no effect. It is clear that this may vary for every titan yellow product;

(*2*) separation as oxalate[5,9,13,26];

(*3*) complex binding by saccharose[14,18];

(*4*) precipitation as tungstate (see under Elimination of interference).

(*b*) *Aluminium.* In most cases a decrease in colour intensity has been recorded [3,11,18,21,33–35], but some investigators have found an increase[17,19]. The interference of aluminium may be eliminated by adding a compensating solution, by precipitation with ammonia and phosphate[13,18], with tungstate, or with acetylacetone and carbon tetrachloride[3,11], or by addition of potassium cyanide and hydroxylamine[16].

(*c*) *Ammonium.* In most cases the influence of ammonium is not mentioned as no ammonium is present in the solution. Ammonium may, however, interfere by preventing the formation of magnesium hydroxide. According to Mazoyer[26] a relatively large quantity of ammonium may be present provided that it is also added to the standard curve. In fact this is a compensating method. The influence of small quantities of ammonium is reduced by working at a higher concentration of sodium hydroxide. When too much ammonium is present, the ammonium can be decomposed by evaporating the solution with concentrated nitric acid. This method should be applied when the magnesium content of soils is determined after soils have been shaken with an ammonium acetate–acetic acid solution.

(*d*) *Phosphate.* Generally phosphate interferes when present above a certain quantity. Drosdorff[12] found an increase in colour intensity, while Gillam[18] noted a decrease. In many procedures phosphate is added to the compensating solution because the interference then reaches a maximum which is constant. With Merck's titan yellow we found a decrease in colour intensity with 0.5 mg of phosphorus pentoxide or more.

(*e*) *Iron.* Iron produces a decrease in colour intensity. The iron may be separated by phosphate precipitation[18], with cupferron[4], or by shaking with acetylacetone–carbon tetrachloride[11,24]. The degree of interference is not the same for every titan yellow product. We found that the influence of iron on Merck's titan yellow is twofold. The iron decreases the colour produced by magnesium, but increases the colour of the blank. Compounds which form complex salts may eliminate the influence of the iron, *e.g.*, acetates, but in this case the sensitivity of the reaction decreases.

(*f*) *Manganese.* Manganese may increase[17,33,36] or decrease[11,19,31] the colour depending on the preparation used. According to Taras[31] manganese must not be present because it destroys the colour. Young and Gill[32] found that manganese had a reaction similar to that of magnesium. At higher manganese concentrations corrections should be made. With Merck's titan yellow an increase in colour intensity was found. Elimination can be obtained by adding a compensating solution.

(*g*) *Elimination of interferences.* It has been shown that various methods are used to eliminate the interference of different cations. Of these the use of a compensation solution requires the least time. This method is, however, open to criticism because the composition of the compensating solution depends on the titan yellow used. It is therefore not possible to specify a particular compensating solution which can be used in all cases, but we recommend sodium tungstate. With this reagent all cations except potassium, sodium and magnesium are precipitated[37]. The slightly acid solution (see METHOD) should be raised to 70–80° before the solution of sodium tungstate is added. The solution is kept at that temperature and shaken occasionally until the precipitate is quantitatively formed. After cooling to room temperature the solution is diluted to volume and filtered. In the filtrate magnesium can be determined. MIKKELSEN, TOTH AND PRINCE[19] also apply the tungstate separation but they add a given amount of phosphate to the tungstate solution because the interference of the phosphate reaches a maximum above a certain amount. We found no interference by phosphate when sodium tungstate was present. This may have been due to the formation of a complex compound of tungstate with phosphate as no phosphate could be detected in the solution.

From the above it can be concluded that the titan yellow method is rather complicated. However, under suitable conditions results are obtained which compare favourably with those of other methods. SHAW[36] compared the titan yellow method with the flame photometric, the EDTA, the magnesium ammonium phosphate and the hydroxyquinoline methods. The best results were obtained with the titan yellow method, but a number of laboratories co-operating in the investigation did not succeed in getting reliable results with titan yellow. SHAW attributes this failure to the use of faulty reagents or the inability to duplicate the original products. It must therefore be emphasized that all factors should be carefully studied with the reagents available.

On the basis of the preceding considerations the following improvements have been introduced:

(*1*) The use of an ample amount of titan yellow. The absorption of titan yellow is thus more complete and small fluctuations in the concentration of the titan yellow solution have no effect.

(*2*) The use of a mixed solution of titan yellow, Nymcel and hydroxylamine hydrochloride. On the one hand this offers a saving of time, on the other hand, the Nymcel is more stable in this mixture than in pure solution.

(*3*) The use of a sodium hydroxide concentration such that the standard curve is a straight line. The reproducibility of the method is thus increased.

(*4*) The choice of the correct speed at which to add the hydroxide solution. When this solution is not added too fast, the standard curve passes the origin and the reproducibility of the method is increased.

(*5*) The introduction of a sodium tungstate separation with which it is possible to eliminate interference from all cations and the phosphate ion.

(*6*) The production of the colours in black-painted flasks to avoid any light effect.

(*7*) The solution is not made up to volume before measuring to avoid changes in the colloidal system.

The results shown in Table III indicate the performance of the method when the above recommendations are followed; known solutions containing 0.250 mg of magnesium were analyzed after interfering ions had been separated with sodium tungstate. With regard to the reproducibility of the method, it can be stated that a standard sample was always analyzed simultaneously with the analysis of routine samples, and the mean value of 24 successive determinations on the standard sample over a period of 2 months amounted to 0.152% magnesium with a standard deviation of 0.007.

TABLE III

DETERMINATION OF MAGNESIUM IN PRESENCE OF INTERFERING ELEMENTS

| *mg Ca* | *mg Fe* | *mg Al* | *mg Mn* | *mg* $P_2O_5$ | *mg Mg found* | *% recovery* |
|---|---|---|---|---|---|---|
| 2.5 | 0.025 | 0.025 | 0.050 | 2.5 | 0.25 | 100 |
| 2.5 | 0.025 | 0.100 | 0.050 | 2.5 | 0.25 | 100 |
| 2.5 | 0.025 | 0.025 | 0.100 | 2.5 | 0.24 | 96 |
| 2.5 | 0.050 | 0.025 | 0.025 | 2.5 | 0.25 | 100 |
| 2.5 | 0.050 | 0.100 | 0.025 | 2.5 | $0.24^5$ | 98 |
| 2.5 | 0.050 | 0.025 | 0.100 | 2.5 | 0.25 | 100 |
| 2.5 | 0.050 | 0.050 | 0.050 | 2.5 | $0.25^5$ | 102 |
| 2.5 | 0.100 | 0.025 | 0.025 | 2.5 | $0.24^5$ | 98 |
| 2.5 | 0.100 | 0.100 | 0.025 | 2.5 | 0.25 | 100 |
| 2.5 | 0.100 | 0.025 | 0.100 | 2.5 | $0.24^5$ | 98 |
| 2.5 | 0.100 | 0.100 | 0.100 | 2.5 | 0.25 | 100 |

## METHOD

### *Reagents*

(*1*) Mixed solution. Mix 1 part of 5% hydroxylamine hydrochloride, 2 parts of 1% Nymcel and 2 parts of 0.1% titan yellow solutions. Keep in the dark in a brown flask. (*2*) 6 *N* Sodium hydroxide solution. (*3*) 5% sodium tungstate solution.

### *Separation of interfering ions*

Place 10 ml of the slightly acid solution containing 0–0.8 mg of magnesium in a 100-ml measuring flask and heat to about 80°. Add 5 ml of the tungstate solution and let the mixture stand at this temperature until precipitation is complete. The precipitate is then at the bottom of the flask and the supernatant liquid is clear. Then cool to room temperature, adjust to volume with water, mix and filter through a fine filter.

### *Colorimetric procedure*

Pipette 50 ml of the clear filtrate into a black-painted 100-ml flask. Into this solution pipette 25 ml of the mixed solution, while swirling gently. Then add slowly 10 ml of the hydroxide solution, while stirring steadily. As the colour produced by magnesium reaches its maximum intensity immediately and the colour of the blank is only constant after 20–30 min, the blank solution is prepared 20–30 min before adding sodium hydroxide to the sample solutions so that readings can take place immediately after adding the hydroxide. The determinations are carried out at 530 mμ in 18-mm colorimeter tubes with the Lumetron photoelectric colorimeter, model No. 401.

## SUMMARY

A study was made of the different factors which influence the colorimetric determination of magnesium with titan yellow, namely, the titan yellow product, the protective colloid, the colour stabilizer and the sodium hydroxide. Interfering elements were separated by precipitation with sodium tungstate. Several improvements were introduced.

## RÉSUMÉ

Une étude a été effectuée sur les différents facteurs pouvant influencer le dosage colorimétrique du magnésium, au moyen de jaune titane. Plusieurs améliorations sont introduites.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss verschiedener Faktoren bei der colorimetrischen Bestimmung von Magnesium mit Titangelb. Es wurden einige Verbesserungen der Methode erzielt.

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# THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM AND VANADIUM WITH *ortho*-DIANISIDINE

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(Received January 2nd, 1961)

The possibility of exploiting redox indicators of the aromatic amine type for the spectrophotometric determination of chromium(VI) and vanadium(V) has been considered, and the oxidation potentials of the various couples involved have been investigated[1-7]. The oxidation of benzidine and its derivatives has been described by OLDFIELD AND BOCKRIS[8]; this proceeds as a two-electron reaction in pH ranges below 2.0 and above 4.0; in the intermediate range, of pH 2-4, the oxidation is a one-electron process, resulting in semiquinoidal products.

For analytical purposes, the lower pH range seems desirable, this being the only range in which these redox systems attain equilibrium; in the higher pH ranges, the hydrolytic tendencies of the semiquinones and the polymerization effects involving the oxidized form tend to disturb equilibrium. In strongly acid media, on the other hand, the redox systems are stable and reversible.

The analytical potentialities of *ortho*-dianisidine (3,3'-dimethoxybenzidine) have been briefly mentioned[9].

In view of these facts, a further study of the applicability of this reagent to the spectrophotometric determination of vanadium and chromium in their higher oxidation states seemed desirable.

## REAGENTS AND SOLUTIONS

(*1*) *Ortho*-dianisidine dihydrochloride (3,3'-dimethoxybenzidine). This is a crystalline solid, soluble in water and acids. Its reduced form is colorless, while its oxidized form is red in strongly acid solutions and green in solutions whose pH is higher than 2.1. The formal oxidation potential reaches its maximum value in solutions more acid than 6 *N* sulfuric acid[8,10]. For the purpose of this investigation, a 1% solution of the reagent was prepared by dissolving 1 g in a small quantity of water containing 2 ml of concentrated acetic acid, stirring vigorously to promote dissolution and making up to 100 ml with distilled water. This reagent solution was then transferred to a polyethylene bottle and stored in a dark place. No change in its activity could be observed within one month of its preparation.

(*2*) Standard chromium(VI) stock solution, containing 1 g of $Cr^{+6}$ per liter, was prepared by dissolving 2.8283 g of dried potassium dichromate in distilled water and making up to 1 l.

(*3*) Standard vanadium(V) stock solution, containing 1 g of $V^{+5}$ per liter, was prepared by dissolving 2.2961 g of ammonium *meta*-vanadate in distilled water and making up to 1 l. The vanadium content of this solution was checked gravimetrically.

(*4*) Iron(III) stock solution, containing approximately 5 g of $Fe^{+3}$ per liter, was prepared by dissolving the appropriate amount of ferric chloride in distilled water.

The above stock solutions were diluted as needed. All the reagents employed were of analytical grade.

## APPARATUS

Absorbance measurements were made with Beckman Model DU and Unicam SP-500 spectrophotometers, in cells of 0.5- and 1.0-cm light path. In order to facilitate comparison of results, all data in this paper have been calculated for 1.0-cm cells.

## DISCUSSION OF RESULTS

### *Absorbance spectra*

The absorbance spectra of solutions containing 5 p.p.m. of vanadium(V) or chromium(VI) and 0.02% reagent were determined in weakly acidic (pH 3.5) medium, while the spectra of solutions containing 1 p.p.m. of the required metal and 0.02% reagent were determined in strongly acidic (10 *N* sulphuric acid) medium. Fig. 1 shows the spectra obtained in the latter medium. *Ortho*-dianisidine reacts similarly with chromium(VI) and vanadium(V) in strongly acid solution; the red reaction product has its maximum absorbance band in the range of 435–455 mμ, the molar absorbancy index obtained for the chromium–excess *ortho*-dianisidine system being 42,000 l/mole/cm and that for the vanadium–excess *ortho*-dianisidine system being 14,000 l/mole/cm. This, and the identical form of the spectra obtained (Fig. 1) prove that the colored reaction product is characteristic of the reagent and inde-

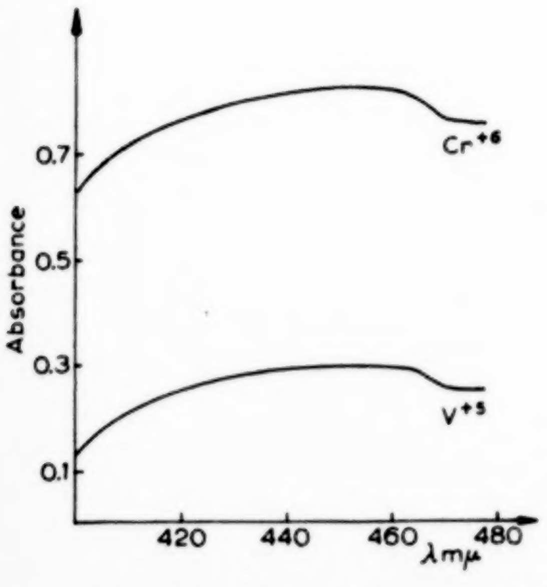

Fig. 1. Absorbance spectra of the chromium(VI)–and the vanadium(V)–*o*-dianisidine systems. 10 *N* $H_2SO_4$; 1 p.p.m. $V^{+5}$; 1 p.p.m. $Cr^{+6}$; light path = 1.0 cm.

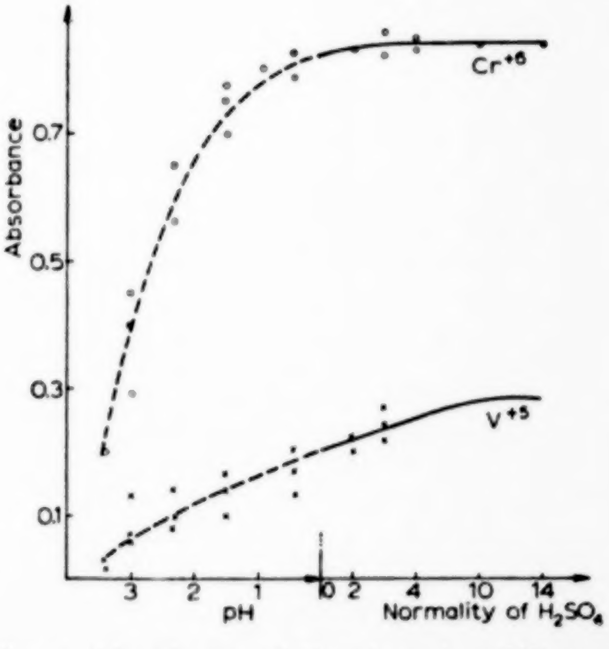

Fig. 2. Absorbance of the chromium(VI)–and the vanadium(V)–*o*-dianisidine systems, as a function of sulfuric acid concentration. 1 p.p.m. $V^{+5}$; 1 p.p.m. $Cr^{+6}$; light path = 1.0 cm; λ = 440 mμ.

pendent of the oxidizing agent. In pH ranges above pH 2.1, the redox equilibria involved are unstable, and hence the above relationship is not fulfilled (Fig. 2).

## *Various factors affecting the absorbance of the chromium–ortho-dianisidine and vanadium–ortho-dianisidine systems*

### (*a*) *Acidity of medium*

The effect of changes in the concentrations of respectively sulphuric acid, phosphoric acid and their mixture, on the absorbance of the systems investigated, was determined by measuring 0.5 ml of stock solution, containing 100 $\mu$g of chromium(VI) or vanadium(V)/ml, into a 50-ml volumetric flask, adding 1 ml of 1% reagent solution and making up to volume with the appropriate acid, diluted as required. Absorbance was measured 30 min after mixing the reagents. (The effect of phosphoric acid was of interest, with a view to its subsequent employment as a masking reagent for any iron present in the samples). Figs. 2 and 3 illustrate the results obtained.

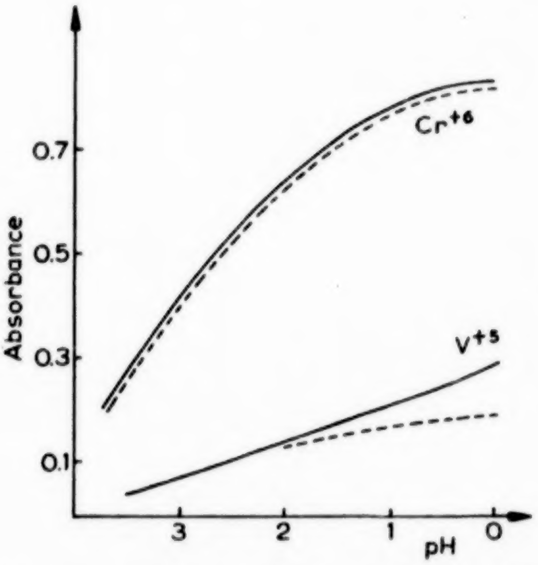

Fig. 3. Absorbance of the chromium(VI)– and the vanadium(V)–*o*-dianisidine systems as a function of phosphoric acid concentration (the broken lines represent the absorbances obtained with equal concentrations of sulfuric acid; compare Fig. 2). 1 p.p.m. $V^{+5}$; 1 p.p.m. $Cr^{+6}$; light path = 1.0 cm; $\lambda$ = 440 m$\mu$.

### (*b*) *The catalytic effect of oxalate ion*[5–7] *on the systems*

This was determined by examining the effect of changing oxalate concentration on the systems involved, and the effect, at a fixed oxalate concentration, of changing pH on the absorbance. In solutions more acid than 0.1 *N* sulphuric acid, the presence of oxalate ion speeds up the reaction between vanadium(V) and the reagent; this effect may also be observed for the chromium–*ortho*-dianisidine system at higher pH values.

### (*c*) *Time effect*

Changes in the absorbance of the systems as a function of time elapsed from the mixing of the reagents were determined for varying concentrations of sulphuric acid present. The time required for maximum color development decreases with increased acidity; the color fades, the rate of fading rising with decreasing acidity. For concentrations of sulfuric acid above 7 *N*, the color remains stable over the period from 10 to 40 min from the moment of mixing the reagents.

### (*d*) *The effect of dilution of the sample prior to the addition of the reagent solution*

This was determined by adding the appropriate amount of distilled water to the sample before the addition of *ortho*-dianisidine solution. Prior dilution results in lowering the absorbance of the chromium-*ortho*-dianisidine system. Best results are obtained by the addition of the reagent to the sample before the introduction of the acid. Table I shows the results obtained.

TABLE I

THE EFFECT OF DILUTION OF THE SAMPLE ON THE ABSORBANCE OF THE CHROMIUM- OR VANADIUM-*ortho*-DIANISIDINE SYSTEM IN SULFURIC ACID

Light path: 1.0 cm; wavelength employed: 440 *mμ*

| *$H_2O$ added to sample ml* | *Approx. final concentration of $H_2SO_4$, N* | *Absorbance of mixture containing 0.02% ortho-dianisidine and:* | |
|---|---|---|---|
| | | *1 p.p.m. $Cr^{+6}$* | *1 p.p.m. $V^{+5}$* |
| 0 | 10.0 | 0.840 | 0.280 |
| 5.0 | 9.0 | 0.750 | 0.280 |
| 10.0 | 8.0 | 0.730 | 0.280 |

### (*e*) *Temperature changes*

This factor was investigated by immersing the volumetric flasks, in which the reagents were mixed, in a thermostated water bath kept at the desired temperature; temperature changes in the range of 15°–35° had no effect on the absorbance of the systems investigated, when the solutions were made up to volume with 10 *N* sulphuric acid; for less acid media, significant changes in the absorbance of the systems could be observed.

### (*f*) *Ultra-violet light*

No change in the absorbance of the systems due to illumination with ultra-violet light was obtained, after exposing the solutions for 10 min to the light of a mercury vapour arc lamp (Hanovia Utility Model), at a distance of approximately 50 cm.

### (*g*) *Reagent concentration*

The effect of varying the concentration of *ortho*-dianisidine present on the absorbance of the systems was investigated by introducing 0.5 ml of chromium(VI) or vanadium(V) stock solution, containing 100 *μg*/ml, into a 50-ml volumetric flask, adding varying amounts of *ortho*-dianisidine solution and making up to volume with 10 *N* $H_2SO_4$. The absorbances, measured 30 min after mixing, are tabulated in Table II. It can be seen that the excess of reagent has no influence on the absorbances.

### (*h*) *Foreign ions*

The presence of a thousandfold excess (by weight) of ammonium chloride, ammo-

TABLE II

THE EFFECT OF REAGENT CONCENTRATION ON THE ABSORBANCE OF THE CHROMIUM – OR VANADIUM–*ortho*-DIANISIDINE SYSTEMS IN 10 $N$ SULFURIC ACID

Light path: 1.0 cm; wavelength employed: 440 mμ

| *Ortho-dianisidine* % | *Reagent: element molar ratio (approx.)* | *Absorbance of mixture containing reagent and:* | |
|---|---|---|---|
| | | *1 p.p.m.* $Cr^{+6}$ | *1 p.p.m.* $V^{+5}$ |
| 0.001 | 0.3 : 1.0 | 0.680 | 0.250 |
| 0.002 | 0.6 : 1.0 | 0.730 | 0.280 |
| 0.01 | 6.0 : 1.0 | 0.840 | 0.280 |
| 0.04 | 24.0 : 1.0 | 0.840 | 0.280 |
| 0.08 | 48.0 : 1.0 | 0.840 | 0.280 |

nium nitrate, sodium nitrate or sodium sulfate had no effect on the absorbance of the systems.

### *Calibration curves*

These were constructed for solutions containing 0.1–10 p.p.m. of vanadium(V) and solutions containing 0.05–5 p.p.m. of chromium(VI), by introducing the appropriate amount of metal ion stock solution into a 50-ml volumetric flask, adding 1 ml of 1% reagent solution, making up to volume with 10 $N$ sulfuric acid and measuring absorbance after 30 min. For chromium concentrations higher than 3 p.p.m., absorbance measurements were carried out by the Precision Colorimetry-Transmittance Ratio Method[11], employing, as reference solution, a potassium dichromate solution whose transmittance *versus* water was: $T_1 = 0.234$. The transmittance of the sample,

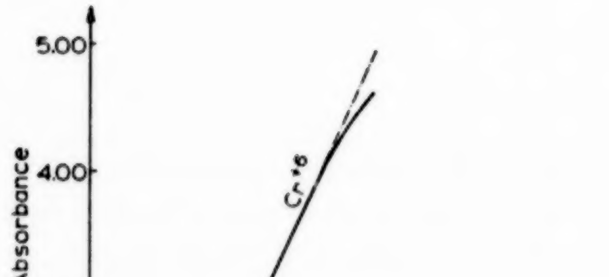

Fig. 4. Calibration curves for chromium(VI) and vanadium(V). Concentrations above 0.5 p.p.m. $\lambda = 440$ mμ. Light path = 1.0 cm.

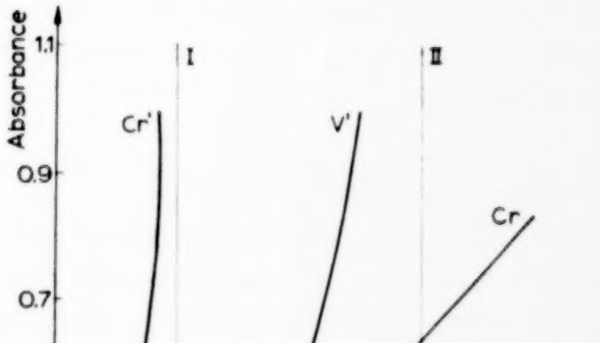

Fig. 5. Calibration curves for chromium(VI) and vanadium(V). Concentrations up to 1 p.p.m. $\lambda = 440$ mμ; light path = 1.0 cm.

$T_s$, was calculated according to the formula: $T_s = RT_1$, where $R$ stands for the transmittance of the sample *versus* the reference solution. Fig. 4 shows the calibration curves obtained. For chromium concentrations lower than 0.3 p.p.m. and vanadium concentrations lower than 0.4 p.p.m., the Precision Colorimetry Trace Analysis Method[11] was employed. The resulting calibration curves are given in Fig. 5; in this figure, the straight lines marked Cr and V were obtained partly by ordinary colorimetry and partly by precision colorimetry (for the lower concentrations mentioned above). The *dark current* was adjusted with a potassium dichromate solution, whose transmittance *vs.* water was: $T_2 = 0.611$, this being equivalent to the absorbance: $D_2 = 0.214$ marked in Fig. 5. The vertical lines: I and II, passing through the intersection points of the line $D_2$ with lines Cr and V, cut the concentration axis at points marking the concentration limits of chromium(VI) and vanadium(V), beyond which the reference solution chosen can no longer be employed. Lines Cr′ and V′ are the absorbance curves obtained for the chromium and vanadium systems, respectively, as measured against the above-mentioned reference solution. The transmittance of the sample, $T_s$, (*vs.* water) was calculated according to the formula: $T_s = R - RT_2 + T_2$.

The systems obey Beer's law in the following concentration ranges: chromium(VI) up to 5 p.p.m.; vanadium(V) up to 15 p.p.m. The employment of Precision Colorimetry allows the method to be applied to solutions containing as little as 0.05 p.p.m. of chromium(VI) and 0.1 p.p.m. of vanadium(V).

### *Mixtures of chromium VI) and vanadium(V)*

The additivity of the absorbances of the chromium–*ortho*-dianisidine and the vanadium–*ortho*-dianisidine systems was checked for solutions containing 1–5 p.p.m. of

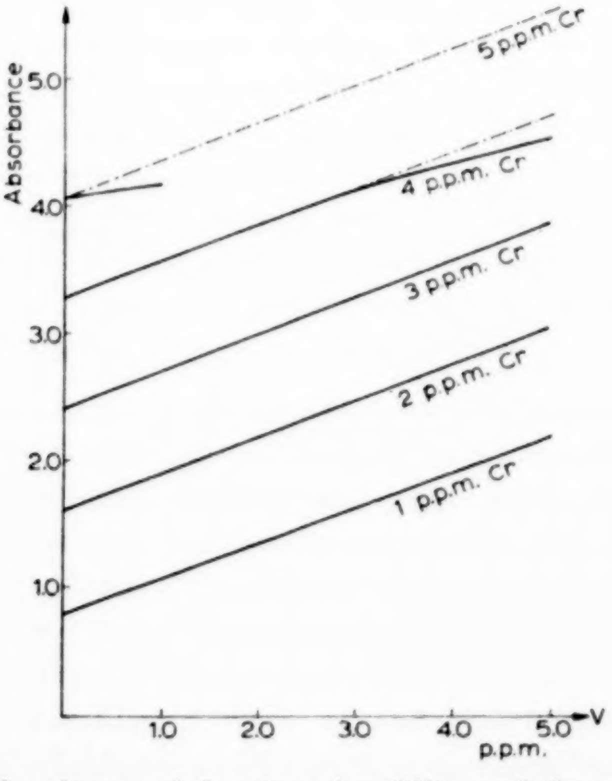

Fig. 6. Additivity of the absorbance of the chromium(VI)– and the vanadium(V)–o-dianisidine systems in 10 *N* sulfuric acid. (The broken lines indicate the absorbance expected in the case of perfect additivity). $\lambda = 440$ m$\mu$; light path = 1.0 cm.

chromium(VI) and 0.5–5 p.p.m. of vanadium(V). Results are given in Fig. 6. The absorbances of chromium and vanadium systems are additive in the range of 0–4,000 (absorbance); this permits the simultaneous determination of both metals in one aliquot of the solution. Vanadium is easily removed from the mixture in a second aliquot by adsorption on a cation exchange resin; chromium passes into the effluent, and may be determined directly with *ortho*-dianisidine, provided that the absorbance obtained is referred to a properly prepared calibration curve (taking account of the dilution effect). For this process, the acidified mixture (pH 2.5 approximately) was passed through a 300- by 5-mm ion exchange column filled with 40–60 mesh Amberlite IR-120 (H) resin, at the rate of 3 ml/min, and the column was washed with 20 ml of distilled water. The effluent and washings, containing the chromium(VI), were collected in a 50-ml volumetric flask and chromium was determined by the usual method. Vanadium is retained in the column[12] and is determined by difference. Owing to the dilution of the sample by the wash liquid, before the addition of the *ortho*-dianisidine, the absorbance of sample must be compared against that of a similarly diluted chromium standard solution. This is marked "comparison solution" in Table III, which summarizes the results obtained by the separation procedure described.

TABLE III

RESULTS OF CHROMIUM–VANADIUM SEPARATION BY ION EXCHANGE

Light path: 1.0 cm; wavelength employed: 444 mμ

| *Metal ion content of mixture p.p.m.* | | *Absorbance after color developmen (due to $Cr^{+6}$ content)* | |
|---|---|---|---|
| $V^{+5}$ | $Cr^{+6}$ | *effluent* | *comparison solution* |
| 0.5 | 5.0 | 3.480 | 3.500 |
| 5.0 | 0.5 | 0.375 | 0.380 |
| 5.0 | 1.0 | 0.740 | 0.750 |
| 5.0 | 3.0 | 2.200 | 2.200 |
| 5.0 | 5.0 | 3.480 | 3.500 |
| 10.0 | 0.5 | 0.370 | 0.380 |
| 10.0 | 5.0 | 3.500 | 3.500 |

This method of separation proved preferable to selective reduction with arsenite[13] or selective extraction, the results obtained being more reproducible and applicable to wider ranges of the chromium : vanadium ratio. In addition, this separation method is useful in the presence of excess ferric ion, which is retained in the column together with the vanadium, and thus does not interfere with the chromium determination.

In the presence of iron(III), the only change necessary is its complexation in the first aliquot, by the addition of 5 ml of concentrated phosphoric acid before the color development; in the determination of chromium, iron does not interfere, as it is quantitatively removed from the mixture (together with the vanadium) by passing the sample through the cation exchange column. Table IV illustrates the efficiency of suppression of iron interference achieved.

### TABLE IV

THE DETERMINATION OF CHROMIUM AND VANADIUM IN THE PRESENCE OF IRON
Light path: 1.0 cm; wavelength employed: 440 mμ

| *Metal ion content of mixture, p.p.m.* | | | *Absorbance measured* | | | |
|---|---|---|---|---|---|---|
| | | | *first aliquot (sum of $Cr^{+6}$ and $V^{+5}$)* | | *second aliquot ($Cr^{+6}$ only)* | |
| $V^{+5}$ | $Cr^{+6}$ | $Fe^{+3}$ | *sample* | *comparison solution*[a] | *sample* | *comparison solution* |
| 1.0 | 1.0 | 50 | 1.105 | 1.110 | 0.735 | 0.740 |
| 1.0 | 1.0 | 100 | 1.110 | 1.110 | 0.735 | 0.740 |

[a] This solution was prepared identically with the sample mixture, but without iron.

## PROCEDURE RECOMMENDED

Based on these results, the following procedure is recommended for the determination of low concentrations of chromium(VI) and vanadium(V), when present (*1*) singly; (*2*) together; (*3*) in the presence of iron(III).

(*1*) The sample solution containing up to 5 p.p.m. of chromium(VI) or up to 15 p.p.m. of vanadium(V), is introduced into a 50-ml volumetric flask, 1 ml of 1% *ortho*-dianisidine reagent is added and the solution is made up to volume with 10 *N* sulfuric acid. The absorbance of this solution is measured 30 min after the moment of mixing the reagents. The metal ion concentration is determined by reference to a previously prepared calibration curve.

(*2*) The mixture is analyzed by carrying out two determinations. (*a*) The absorbance caused by the sum of the chromium and vanadium present is measured after developing the color with *ortho*-dianisidine in one aliquot as described under (*1*) (*b*) An equal aliquot is acidified with a few drops of 0.5 *N* sulfuric acid to about pH 2.5, and passed through a cation exchange column filled with Amberlite IR-120 (H) resin. The column is subsequently washed with 20 ml of distilled water (the rate of flow is about 3 ml/min, for a 5- × 300-mm column, filled with 40–60 mesh resin). The effluent and washings are collected into a 50-ml volumetric flask, 1 ml of 1% reagent solution is added and the volume made up with 10 *N* sulfuric acid. The absorbance is measured 30 min after the moment of mixing the reagents and the chromium concentration determined by reference to an appropriate calibration curve. The absorbance of vanadium(V) is obtained by difference:

$$A_{V^{+5}} = A_{sum} - A_{Cr^{+6}}$$

and its concentration by reference to an appropriate calibration curve.

(*3*) One aliquot, containing chromium(VI), vanadium(V) and iron(III) is treated as under (*1*), except for the addition of 5 ml of concentrated phosphoric acid to the sample before the addition of the sulfuric acid; the absorbance measured in this aliquot results from the sum of the chromium and vanadium present. A second aliquot is treated as described under (*2b*) for the determination of chromium(VI) alone.

The time required for the analysis of a mixture containing both chromium(VI) and vanadium(V) is 40 min approximately (a series of 3 samples may be analyzed within this period); for samples containing either ion alone, up to 10 determinations may be completed during this time.

Table V contains some of the results obtained; as may be seen, these are satisfactory, the maximum relative error not exceeding ± 6%.

TABLE V

EVALUATION OF THE PROPOSED SPECTROPHOTOMETRIC METHOD BY COMPARISON OF THE RESULTS OBTAINED WITH THE THEORETICAL VALUES

| *Metal ion* | *Chromium(VI)* | | | *Vanadium(V)* | | |
|---|---|---|---|---|---|---|
| Concentration according to proposed method, p.p.m. | 0.101 | 1.000 | 5.024 | 0.097 | 0.996 | 4.956 |
| | 0.099 | 0.978 | 4.948 | 0.097 | 0.989 | 4.960 |
| | 0.095 | 1.013 | 4.821 | 0.090 | 0.996 | 4.984 |
| | 0.104 | 1.027 | 4.900 | 0.093 | 1.002 | 4.860 |
| | 0.103 | 1.002 | 5.123 | 0.110 | 0.996 | 5.020 |
| | 0.104 | 0.988 | 4.850 | 0.110 | 1.011 | 5.180 |
| | 0.095 | 0.978 | 4.950 | 0.104 | 1.011 | 4.925 |
| Average of above values, p.p.m. | 0.100 | 0.998 | 4.947 | 0.100 | 1.000 | 4.984 |
| Theoretical concentration, p.p.m. | 0.100 | 1.000 | 5.000 | 0.100 | 1.000 | 5.000 |
| Standard Deviation, % | 4.0 | 1.8 | 1.6 | 8.0 | 0.8 | 1.5 |

## SUMMARY

A spectrophotometric method for the determination of chromium(VI) and vanadium(V), when present singly or together, in presence or absence of iron(III), has been developed, by exploiting the color changes which result from the oxidation in strongly acid medium of *ortho*-dianisidine by these metal ions.

## RÉSUMÉ

Une méthode spectrophotométrique est décrite pour le dosage du chrome(VI) et du vanadium(V), en présence de fer(III). Elle est basée sur la coloration résultant de l'oxydation de l'*o*-dianisidine par ces deux ions.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Chrom-(6) und Vanadium-(5) in Gegenwart von Eisen-(3). Sie beruht auf der Oxydationswirkung dieser Ionen auf *o*-Dianisidin, wobei eine Farbänderung eintritt.

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# A STUDY OF SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

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(Received January 3rd, 1961)

1,10-Phenanthroline is used for the colorimetric estimation of ferrous iron and an equimolecular mixture of ferrous iron and phenanthroline or some of its derivatives has been recommended as an oxidation-reduction indicator. A knowledge of the effect of substituents on the chemical behaviour of this organic reagent is therefore of considerable analytical interest.

A large number of substituted phenanthrolines have been prepared. Qualitative investigation of the effect of substitution by methyl groups in the phenanthroline ring upon the stability of the ferrous complex has been made and the influence of the methyl substitution on the oxidation-reduction potentials of the phenanthroline complexes with ferrous iron recorded[1]. Oxidation-reduction potential data have been reported for two hydroxy-substituted phenanthroline complexes[2] and for four 5-substituted derivatives[3].

Stability constants have been calculated for the complexes of iron(II) with 1,10-phenanthroline substituted in the "benzene" ring[4]. Investigations have now been made on the effect of substitution in the "pyridine" rings on the stability of the ferrous complex.

## EXPERIMENTAL

### *Preparation of ligands*

Only relatively small quantities of ligands were needed. A few new compounds are described here for the first time but the remainder were prepared by existing methods as indicated.

### *1,10-Phenanthrolines substituted in one pyridine ring only*

3-Carbethoxy-4-hydroxy-1,10-phenanthroline, 4-hydroxy-1,10-phenanthroline and 4-chloro-1,10-phenanthroline were prepared using the method of SNYDER AND FREIER[5]. These authors were not able to obtain a pure specimen of the chloro derivative but the crude material precipitated by ammonia could be purified by extraction with alcohol. On removal of the solvent, the residue after recrystallisation from benzene afforded pale yellow needles of 4-chloro-1,10-phenanthroline, m.p. 165–166°. (Found: N, 12.97; Cl, 16.41; $C_{12}H_7N_2Cl$ requires N, 13.06; Cl, 16.52.)

The preparation of 4-cyano-1,10-phenanthroline was based on a method described for the conversion of certain heterocyclic chloro derivatives to the cyanide via the sulphonate[6]. 4-Chloro-1,10-phenanthroline (1.86 g), anhydrous sodium sulphite (1.09 g) and water (18 ml) were refluxed for 6 h. The solid left on evaporation to dryness was mixed with potassium cyanide (0.56 g) and fused under reduced pressure to give a yellow solid, m.p. 245° (0.3 g, 17%). Recrystallisation from methanol gave pale yellow needles of 4-cyano-1,10-phenanthroline, m.p. 251°. (Found: C, 76.2; H, 3.6. $C_{13}H_7N_3$ requires C, 76.1; H, 3.45%).

The preparation of 4-hydroxy-2-methyl-1,10-phenanthroline and 4-chloro-2-methyl-1,10-phenanthroline was based on the method suggested in a patent[7]. The specimen of 4-chloro-2-methyl-1,10-phenanthroline melted at 142° after recrystallisation from aqueous alcohol (lit. 136–137°) (found: C, 68.2; H, 3.9; Cl, 15.5; N, 12.4. $C_{13}H_9N_2Cl$ requires C, 68.3; H, 3.95; Cl, 15.5; N, 12.25%).

### *1,10-Phenanthrolines substituted in both pyridine rings*

3,8-Dicarbethoxy-4,7-dihydroxy-1,10-phenanthroline, 4,7-dihydroxy-1,10-phenanthroline and 4,7-dichloro-1,10-phenanthroline were also prepared by the methods proposed by SNYDER AND FREIER[5].

4,7-Dicyano-1,10-phenanthroline was prepared in 9% yield in a similar way to the preparation of 4-cyano-1,10-phenanthroline. It formed pale yellow needles from alcohol, m.p. 284°. There was insufficient for analysis.

## *Determination of stability constants*

Stability constants for the complexes of ferrous iron with the above derivatives of 1,10-phenanthroline were determined spectrophotometrically. The optical density measurements were made on a Unicam S.P. 500 spectrophotometer using solutions prepared by mixing hydroxylamine solution, sodium acetate buffer, ligand and ferrous perchlorate in this order. The final solutions were $6 \cdot 10^{-3}$ $M$ in respect to hydroxylamine and the ionic strength of the solution was adjusted to 0.1 with the sodium acetate. The ferrous iron concentration was varied from $1.5 \cdot 10^{-5}$ $M$ to $2 \cdot 10^{-4}$ $M$ and the ligand concentration was varied between $10^{-5}$ and $10^{-3}$ $M$.

Time studies indicated that equilibrium was rapidly obtained except in the cases of 4-hydroxy- and 3-carbethoxy-4-hydroxy-1,10-phenanthrolines where delays of 16 h and 2 h respectively were allowed for equilibrium to be established.

The calculated stability constants for the various complexes are recorded in Table I together with values taken from the literature for other substituted derivatives.

p$K$ of $HL^+$ values for the various compounds are also recorded in Table I. The p$K$ values for 1,10-phenanthroline ($\mu$ 0.1) and the 4-hydroxy derivative were determined potentiometrically using a Cambridge precision pH meter while the values for the 4-chloro, 4-cyano and 4-chloro-2-methyl derivatives were estimated spectrophotometrically using a Uvispek Mark V Spectrophotometer. Other values were obtained from the literature.

The recorded stability constants are of comparative value only, since no corrections were made for activity coefficients or the possible presence of traces of ferric iron. The calculated value of log $\beta_3$ for the 1,10-phenanthroline complex (18.5) therefore lies closer to the early value of DWYER AND NYHOLM[8] (17.1) in which similar assumptions were made, than it does to the accepted value of 21.3[9]. This simplification was made since the aim of the investigation was to observe the effect of substitution in the 'pyridine' ring rather than determine absolute values and because four of the ligands were insoluble in water. These ligands were therefore added to the ferrous

TABLE I

RELATIVE STABILITIES OF COMPLEXES FORMED BY DERIVATIVES OF 1,10-PHENANTHROLINE AND IRON(II)

| *Ligand* | *Conditions* | *log* $\beta_3$ | $pK$ *of* $HL^+$ | $\lambda$ *max* | $E_M$ |
|---|---|---|---|---|---|
| 1,10-phenanthroline | $\mu$ 0.1, $H_2O$ | 18.5 | 5.07 | 510 | 11,200 |
| 4-hydroxy-1,10-phenanthroline | $\mu$ 0.1, $H_2O$ | 11.7 | 2.17 | 544 | 10,200 |
| 4-chloro-1,10-phenanthroline | $\mu$ 0.1, $H_2O$ | 14.8 | 4.30 | 518 | 12,700 |
| 4-cyano-1,10-phenanthroline | $\mu$ 0.1, alcoholic solution | 15.1 | 3.60 | 558 | 15,100 |
| 4,7-dichloro-1,10-phenanthroline | $\mu$ 0.1, alcoholic solution | 12.1 | 3.03[12] | 522 | 15,200 |
| 3-carbethoxy-4-hydroxy-1,10-phenanthroline | $\mu$ 0.1, alcoholic solution | 13.0 | — | 561 | 11,500 |
| 4-chloro-2-methyl-1,10-phenanthroline | $\mu$ 0.1, alcoholic solution | 4.9[a] | 4.57 | 465 | 600 |
| 1,10-phenanthroline | 50% alcoholic solution | 16.2 | 4.27[13] | 510 | 12,500 |
| 1,10-phenanthroline | $\mu \to 0$ | 21.2[9] | 4.96[9] | 510 | |
| 2-methyl-1,10-phenanthroline | | 10.8[9] | 5.42[9] | 440 | |
| 5-nitro-1,10-phenanthroline | | 17.8[4] | 3.57[4] | 510 | 11,500 |
| 5-chloro-1,10-phenanthroline | | 19.7[4] | 4.26[4] | 512 | 11,700 |
| 5-methyl-1,10-phenanthroline | | 22.3[4] | 5.23[4] | 515 | 12,200 |
| 5-phenyl-1,10-phenanthroline | | 21.1[4] | 4.80[4] | 515 | 11,000 |
| 4-methyl-1,10-phenanthroline | | | | 511 | 13,000 |
| 4-bromo-1,10-phenanthroline | | | 4.03[12] | | |

$$\beta_3 = \frac{[\mathrm{Fe(phen)_3}]}{[\mathrm{Fe^{+2}}]\,[\mathrm{phen}]^3}$$

[a] value recorded is for log $\beta_2$

solution in alcoholic solution and the presence of alcohol can have a marked effect on the log $\beta_3$ value as shown by the drop in the estimated value for 1,10-phenanthroline (18.5 to 16.2) obtained on using 50% alcohol as the solvent.

## DISCUSSION

An extensive review of the chelate complexes of 1,10-phenanthroline and related compounds has been published[10] and by analogy with other systems, it was suggested that there should be a relationship between the proton-binding capacity of a substituted derivative and the stability of its metal complex. Thus substitution of electrophilic bromo or nitro groups in the 4,7-positions in phenanthroline should merely lower the base strengths and hence reduce the stabilities of the metal complexes. In the same way, methyl substituents in these positions should increase the stabilities. This property of several 5-substituted phenanthrolines has been determined[4]. A qualitative investigation of the effect of substitution of methyl groups upon the stability of the corresponding ferrous complexes has been made[1]. The results indicated that a methyl group in the 4- and 7-positions caused the greatest increase in stability, the 5,6-positions being somewhat less effective. The 3,8-positions caused some apparent decrease in stability. Substitution in the 2,9-positions has effects which are not consistent with an explanation due to basicity.

The results obtained in this study, based on substitution in the pyridine rings, also cannot be fully explained solely in terms of basicity of the co-ordinating group.

A study of Table I indicates that many of the variations in stability of the ferrous complex can be related to changes in the basicity of the ligand.

If a negative inductive group, such as the bromo-, chloro- or cyano-group is introduced into the phenanthroline molecule, the basicity is reduced and the stability constant value also decreases. Substitution in the 4-position could be expected to have more effect than substitution in the 5-position because of the increase in length of the resonance path in the latter compound.

The relationship between reduced basicity and ferrous complex stability for nitro and cyano substituted compounds cannot be explained only in terms of the inductive effect of the substituent group and the contribution of the mesomeric effect of these groups has to be taken into consideration. The increase in stability over that predicted from the basicity of the ligand may be attributed to an increase in the $\pi$-bond character of the iron–nitrogen bond through back-donation of electrons from the iron(II).

The introduction of a hydroxyl group also lowers the basicity but the stability of the complex is now influenced partially by the tautomeric forms which can exist with 4-hydroxy substitutions[11]. By analogy with the quinoline system[11], the "amide" form can be predicted to predominate in solution. Since equilibrium during ferrous complex formation was but slowly attained (16 h), complex formation can be predicted to proceed via the "enol" form and the measured stability constant will include a factor based on the equilibrium constant for the 'enol'-'amide' transformation.

The introduction of a carbethoxy group into the 3-position appears to favour the formation of the "enol" form since equilibrium was obtained in under two hours using 3-carbethoxy-4-hydroxy-1,10-phenanthroline. The introduction of the carbethoxy group to the hydroxy derivative also resulted in an increase in value for the stability constant (11.7 to 13.0). This increase may be explained in terms of a combined inductive and mesomeric effect similar to that invoked to explain the behaviour of the nitro and cyano derivatives.

A further factor which must be considered in relating complex stabilities with ligand basicities is the possibility of steric hindrance. The introduction of a methyl group into the 2-position increases the basicity of the ligand but the stability of the iron(II) complexes is markedly reduced. From Table I, it can be seen that the log $\beta_3$ values for the iron(II) complexes of 1,10-phenanthroline and 2-methyl-1,10-phenanthroline are 21.3 and 10.8, and for 4-chloro-1,10-phenanthroline and 4-chloro-2 methyl-1,10-phenanthroline are 14.8 and 4.9 respectively. 2,9-Dimethyl-1,10-phenanthroline does not form a coloured complex with iron(II).

## CONCLUSIONS

In order to produce organic reagents with the required properties for a specific purpose, a knowledge of the possible effects of substituents on the stability of metal complexes formed with the reagent is highly desirable. This study has confirmed the general relationship that stability can be related to the basicity of the ligand and this basicity may be varied by introducing substituents of varying inductive strength. However, the study has also emphasised that the final equilibrium may be influenced by effects due to mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance. All these factors must therefore be considered in predicting the behaviour of derivatives of organic chelating compounds.

## ACKNOWLEDGEMENTS

The assistance of H. SATRAPA in determining some of the p$K_a$ values is acknowledged with thanks.

## SUMMARY

Six derivatives of 1,10-phenanthroline have been prepared in which the substituents are present in the 'pyridine' ring. The relative stabilities of the complexes formed by these compounds with iron(II) have been determined spectrophotometrically, and have been related to the basicity of the ligands. It was found that stability was related to this basicity but other effects such as the mesomeric properties of the substituent group, tautomerism of the substituted molecule and steric hindrance were also significant.

## RÉSUMÉ

Six dérivés de la 1,10-phénanthroline ont été préparés. Une étude spectrophotométrique a été effectuée sur la stabilité des complexes formés entre ces composés et le fer(II).

## ZUSAMMENFASSUNG

Die Fe(II)-Komplexe von 6 verschiedenen, im "Pyridinring" substituierten 1,10-Phenanthrolinderivaten wurden spektrophotometrisch untersucht. Es wurde festgestellt, dass die Stabilität dieser Komplexe von der Natur des Substituenten und von sterischen Effekten beeinflusst wird.

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# THE EFFECT OF FOREIGN IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF BORON WITH 1,1'-DIANTHRIMIDE

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(Received January 13th, 1961)

## INTRODUCTION

ELLIS, ZOOK AND BAUDISCH[1] suggested the use of 1,1'-dianthrimide for the determination of boron. The reagent was introduced in 1949, and has since proved to be one of the best reagents available for spectrophotometric determination of small amounts of boron. Different authors have employed 1,1'-dianthrimide for the determination of boron in plant and animal materials[1-7], soils[5,6,8-10] and metallurgical products[11-15]; other publications[16-18] deal with the composition and stability of the boron-1,1'-dianthrimide complex, and with the effect of concentration of sulfuric acid, heating temperature and heating time on the development of the colour.

Products such as plant and animal materials, soils, etc., contain a great diversity of elements. For the determination of boron in these and other materials it is of importance to know the interfering effect of all foreign ions that may be present. A survey of the literature on the determination of boron with 1,1'-dianthrimide showed that quantitative data on the influence of foreign elements are lacking. The present investigation was started to procure such data for about 40 inorganic ions, and at the same time to obtain information as to the type of interference present.

## APPARATUS AND REAGENTS

All extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000-cm glass cells.

1,1'-Dianthrimide, concentrated sulfuric acid (95-97%) and other chemicals were of reagent grade quality. The 1,1'-dianthrimide was recrystallized twice from nitrobenzene. Ordinary distilled water from an all-metal still was used.

The solutions were normally prepared and heated in 50-ml bottles (Jena Geräteglas) with ground glass stoppers. Some solutions containing fluoride ions were heated in 50-ml porcelain crucibles glazed inside and out and equipped with porcelain covers.

The solutions were heated in a thermostatically controlled drying oven of standard construction.

### *Standard solutions*

The strength of the stock solution of sulfuric acid was found volumetrically to be 96.8%. Precautions were taken to prevent the acid from absorbing water vapour. A standard solution of 1,1′-dianthrimide was prepared by dissolving 0.500 g in 96.8% sulfuric acid and diluting to 1 l with the same acid. The solution was stored in an automatic burette and was protected against light and humidity. A boron standard solution was prepared by dissolving 0.5715 g of boric acid ($H_3BO_3$) in 96.8% sulfuric acid and diluting to 1 l with the same acid; 50 ml of this solution were diluted to 1 l with 96.8% sulfuric acid. The latter standard solution contained 0.005 mg of boron per ml.

## EXPERIMENTAL

### *Preparation of solutions*

For the extinction measurements two identical solutions were prepared by pipetting into two 50-ml bottles 1 ml of an aqueous solution of the foreign ion to be tested, 1 ml of boron standard solution ($5 \cdot 10^{-6}$ g of boron), 11 ml of 96.8% sulfuric acid and 5 ml of 1,1′-dianthrimide standard solution (2.5 mg of 1,1′-dianthrimide). The blank solution contained 1 ml of the same aqueous solution of the foreign ion, 12 ml of 96.8% sulfuric acid and 5 ml of 1,1′-dianthrimide standard solution. The final volume of the solutions was 17.6 ml, and the final concentration of acid was 93.8%. Some foreign ions were added as solid salts. In Table I these cases are marked (*s*). Phosphoric acid was added according to the formula ($1-x$) ml of water + $x$ ml of 85% orthophosphoric acid. All solutions were finally heated for 16 h at 70°.

### *Reduction and oxidation*

To some solutions reducing or oxidizing agents were added. For reducing purposes 150 mg of hydrazine sulphate were added as the solid salt before the addition of 1,1′-dianthrimide, and the solution was heated in the drying oven for 1 h at 110°. After cooling the 5 ml of 1,1′-dianthrimide standard solution were added and the solution was finally heated for 16 h at 70°.

To destroy organic materials 450 mg of ammonium persulphate were added as the solid salt before the addition of 1,1′-dianthrimide and the solution was heated for 1 h at 110°. After cooling, excess of oxidizing agent was destroyed by adding 150 mg of hydrazine sulphate and heating for 1 h at 110°. Finally, 5 ml of 1,1′-dianthrimide standard solution were added and the solution was heated for 16 h at 70°.

In Table I the addition of reducing and oxidizing agents are marked (red) and (ox), respectively.

### *Extinction measurements*

The extinctions of the two identical solutions containing added boron were measured at 630 mμ (the absorption maximum of the boron 1,1′-dianthrimide complex) against the blank solution. In this way the effect of the foreign ion on the determination of a known amount of boron was established. Further the extinction of the blank solution was measured at 500, 570, 630 and 670 mμ against 96.8% sulfuric acid. By these measurements conclusions could be drawn whether any observed increase of extinction was due to complex formation between the foreign ion and 1,1′-dianthrimide, or to the presence of traces of boron originating from the reagents or the glass. In Table I the results of the measurements are given.

TABLE I

EFFECT OF FOREIGN IONS ON THE COMPLEX FORMATION OF BORON WITH 1,1′-DIANTHRIMIDE

All sample solutions contained: foreign ion +0.005 mg of boron +2.5 mg of 1,1′-dianthrimide in 17.6 ml of 93.8% sulfuric acid. All blank solutions contained: foreign ion +2.5 mg of 1,1′-dianthrimide in 17.6 ml of 93.8% sulfuric acid

| *Ion* | *mg added* | *Added as* | *Average extinction at 630 mμ (E·1000) of 2 sample solutions* | *Expected extinction after correction* | *% diff.* | *pRI*[a] | *Extinction of blank solutions (E·1000) at the wavelengths (in mμ)* | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 500 | 570 | 630 | 670 |
| — | — | In glass bottle (0.0025 mg of boron) | 250.5 | | | | | | | |
| — | — | In glass bottle | 499.5 | | | | | | | |
| — | — | In glass bottle | 498.5 | | | | | | | |
| — | — | In glass bottle[p] | 490.5 | | | | | | | |
| — | — | In crucible | 499.5 | | | | | | | |
| — | — | In crucible | | | | | 80 | 82 | 74 | 74 |
| — | — | In glass bottle $b_1$ | | | | | 80 | 84 | 78 | 79 |
| — | — | In glass bottle $b_1$ | | | | | 80 | 85 | 78 | 78 |
| — | — | In glass bottle $b_1$ | | | | | 84 | 86 | 76 | 76 |
| — | — | Average for bottle $b_1$ | | | | | 81 | 85 | 77 | 78 |
| — | — | In glass bottle $b_2$ | | | | | 116 | 119 | 106 | 95 |
| — | — | In glass bottle $b_2$ | | | | | 114 | 117 | 105 | 94 |
| — | — | In glass bottle $b_4$ | | | | | 95 | 104 | 101 | 92 |
| — | — | In glass bottle $b_5$ | | | | | 106 | 111 | 105 | 94 |
| — | — | In glass bottle $b_6$ | | | | | 105 | 107 | 101 | 91 |
| $N_2H_4 \cdot H_2SO_4$ | 400 | $N_2H_4 \cdot H_2SO_4$(s) | 493.5 | 499 | —1.1 | (6.9) | 86(24) | 71 | 74 | 75(—1) |
| $N_2H_4 \cdot H_2SO_4$ | 400 | $N_2H_4 \cdot H_2SO_4$(s) $b_3$ | | | | | 118(2) | 119 | 106 | 91(0) |
| $(NH_4)_2S_2O_8$ | 450 | $(NH_4)_2S_2O_8$ (s) (red) | 487 | 497 | —2.0 | (6.7) | 86(—2) | 92 | 71 | 72(—2) |
| $NH_2OH \cdot HCl$ | 100 | $NH_2OH \cdot HCl$ (s) $b_3$ | | | | | 115(1) | 117 | 105 | 93(—1) |
| $H_2O$ | 500 | $H_2O$[q] | 479 | 492 | —2.6 | (6.6) | | | | |
| $H_2SO_4$ | 500 | calc. as dilution | | | —1.5 | (6.8) | | | | |
| $Ag^+$ | 2 | $Ag_2SO_4$ | 503 | 499 | 0.8 | >4.3 | 86(2) | 87 | 75 | 75(—2) |
| $Al^{+3}$ | 5 | $KAl(SO_4)_2 \cdot 12H_2O$ | 498.5 | 499 | —0.1 | >4.7 | 89(—2) | 92 | 75 | 76(—1) |
| $As^{+3}$ | 5 | $As_2O_3$ $b_2$ | | | | | 118(—1) | 122 | 108 | 97(1) |
| $Ba^{+2}$ | 50 | $BaCl_2 \cdot 2H_2O$ | 500 | 499 | 0.2 | >5.7 | 86(1) | 88 | 76 | 77(0) |
| $Bi^{+3}$ | 1 | $Bi(NO_3)_3 \cdot 5H_2O$(red)[p] | 493 | 488.5 | 0.9 | >4.0 | 97(2) | 103 | 99 | 91(—1) |
| $Ca^{+2}$ | 100 | $Ca(OH)_2$ (s) | 499.5 | 499 | 0.1 | >6.0 | 80(15) | 73 | 74 | 75(—1) |
| $Ca^{+2}$ | 100 | $Ca(OH)_2$ (s) $b_3$ | | | | | 123(0) | 128 | 118 | 103(1) |
| $Cd^{+2}$ | 50 | $CdSO_4$ | 500 | 499 | 0.2 | >5.7 | 93(—2) | 97 | 80 | 81(1) |
| $Co^{+2}$ | 20 | $CoSO_4 \cdot 7H_2O$ | 499.5 | 499 | 0.1 | >5.3 | 196(1) | 246 | 86 | 80(0) |
| $Co^{+2}$ | 20 | $CoSO_4 \cdot 7H_2O$ without 1,1′-dianthrimide | | | | | 104 | 153 | 10 | 3 |

| Ion | mg added | Added as | Average extinction at 630 mμ (E·1000) of 2 sample solutions | Expected extinction after correction | % diff. | pRI$^{a}$ | Extinction of blank solutions (E·1000) at the wavelengths (in mμ) 500 | 570 | 630 | 670 |
|---|---|---|---|---|---|---|---|---|---|---|
| Cr$^{+3}$ | 10 | $(Cr(H_2O)_4Cl_2)Cl \cdot 2H_2O$ | 499 | 499 | 0 | >5.0 | 233(—5) | 127 | 250 | 319(—4) |
| Cr$^{+3}$ | 10 | $(Cr(H_2O)_4Cl_2)Cl \cdot 2H_2O$ without 1,1′-dianthrimide | | | | | 150 | 33 | 167 | 241 |
| Cu$^{+2}$ | 20 | $CuSO_4 \cdot 5H_2O$ | 500.5 | 499 | 0.3 | >5.3 | 86(0) | 89 | 85 | 104(—1) |
| Cu$^{+2}$ | 20 | $CuSO_4 \cdot 5H_2O$ without 1,1′-dianthrimide | | | | | 3 | 3 | 10 | 28 |
| Fe$^{+2}$ | 20 | $FeSO_4 \cdot 7H_2O$ (red) | 495 | 497 | —0.4 | >5.3 | 95(3) | 94 | 77 | 77(—1) |
| Ge$^{+4}$ | 1 | $GeO_2$(in 0.5% NaOH) $^{p}$ | 445 | 490.5 | —9.1 | 3.3 | 235(76) | 351 | 713 | 761(286) |
| Ge$^{+4}$ | 1 | $GeO_2$(in 0.5% NaOH) +0.1g of $NH_2OH \cdot HCl$ b$_3$ | | | | | 119(2) | 119 | 106 | 95(0) |
| Ge$^{+4}$ | 1 | $GeO_2$(in 0.5% NaOH)(red)b$_3$ | | | | | | | 739 | |
| Ge$^{+4}$ | 0.1 | $GeO_2$(in 0.5% NaOH) | | | | | 111(10) | 131 | 172 | 172(35) |
| K$^{+}$ | 20 | $K_2SO_4$ | 497.5 | 499 | —0.3 | >5.3 | 83(—2) | 88 | 76 | 77(0) |
| Li$^{+}$ | 10 | $LiSO_4 \cdot H_2O$ | 495 | 499 | —0.8 | >5.0 | 88(1) | 90 | 81 | 80(0) |
| Mg$^{+2}$ | 20 | MgO(in 5% $H_2SO_4$) | 498.5 | 499 | —0.1 | >5.3 | 191(4) | 253 | 341 | 247(4) |
| Mg$^{+2}$ | 20 | $MgSO_4 \cdot 7H_2O$ | | | | | 91(0) | 92 | 80 | 80(0) |
| Mn$^{+2}$ | 10 | $MnSO_4 \cdot 4H_2O$ | 499 | 499 | 0 | >5.0 | 88(0) | 91 | 78 | 78(—1) |
| Na$^{+}$ | 130 | NaCl | 502.5 | 499 | 0.7 | >6.1 | 79(0) | 83 | 76 | 77(0) |
| Nb$^{+5}$ | 1 | Nb$^{+5}$(ox) + (red)$^{r}$ | 488 | 487 | 0.2 | >4.0 | 82(0) | 86 | 76 | 77(0) |
| Ni$^{+2}$ | 20 | $NiSO_4 \cdot 6H_2O$ | 495.5 | 499 | —0.7 | >5.3 | 99(—1) | 89 | 78 | 86(0) |
| Ni$^{+2}$ | 20 | $NiSO_4 \cdot 6H_2O$ without 1,1′-dianthrimide | | | | | 18 | 4 | 4 | 10 |
| Pb$^{+2}$ | 1 | $Pb(NO_3)_2$ (red)$^{p}$ | 491 | 488.5 | 0.5 | >4.0 | 92(0) | 101 | 100 | 92(0) |
| Si$^{+4}$ | 1 | $Na_2SiO_3 \cdot 9H_2O$ $^{p}$ | 489 | 490.5 | 0.3 | >4.0 | 99(2) | 105 | 100 | 91(0) |
| Sn$^{+2}$ | 20 | $SnCl_2 \cdot 2H_2O$ | 497.5 | 499 | 0.3 | >5.3 | 75(—1) | 81 | 77 | 78(0) |
| Ta$^{+5}$ | 0.8 | Ta$^{+5}$ (ox) + (red) $^{p,r}$ | 482 | 478.5 | 0.7 | >3.9 | 94(—2) | 107 | 108 | 99(2) |
| Ti$^{+4}$ | 1 | Ti$^{+4}$ (ox) + (red) $^{p}$ | 477.5 | 478.5 | 0.2 | >4.0 | 130(—6) | 149 | 141 | 110(—7) |
| Tl$^{+}$ | 10 | $Tl_2SO_4$ $^{p}$ | 490.5 | 490.5 | 0 | >5.0 | 99(2) | 106 | 101 | 91(—1) |
| Zn$^{+2}$ | 50 | $ZnSO_4$$^{s}$ | 499 | 499 | 0 | >5.7 | 81(—2) | 86 | 75 | 76(—1) |
| Te$^{+4}$ | 1 | $TeO_2$ (in 0.5% NaOH) b$_5$ | | | | | 218(—24) | 268 | 257 | 194(5) |
| Te$^{+4}$ | 1 | $TeO_2$ (in 0.5% NaOH) +0.1g $NH_2OH \cdot HCl$ b$_2$ | | | | | 122(3) | 122 | 108 | 96(0) |
| Te$^{+4}$ | 1 | $TeO_2$ (in 0.5% NaOH) (red) b$_5$ | | | | | | | 250 | |
| Se$^{+4}$ | — | $SeO_2$ (in 0.5% NaOH)$^{t}$ | — | — | | | | | — | |
| Br$^{-}$ | 50 | KBr (red) $^{p}$ | 443 | 488.5 | —9.1 | 5.0 | 503(—143) | 777 | 837 | 562(10) |
| Br$^{-}$ | 0.5 | KBr (red) b$_6$ | | | | | 116(—4) | 125 | 121 | 101(—2) |

(Continued on next page)

TABLE I (continued)

| *Ion* | *mg added* | *Added as* | *Average extinction at 630 mμ (E·1000) of 2 sample solutions* | *Expected extinction after correction* | *% diff.* | *pRI*[u] | *Extinction of blank solutions (E·1000) at the wavelengths (in mμ)* | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 500 | 570 | 630 | 670 |
| $Cl^-$ | 200 | NaCl | 502.5 | 499 | 0.7 | >6.3 | 79(0) | 83 | 76 | 77(0) |
| $Cr_2O_7^{-2}$ | 0.01 | $K_2Cr_2O_7$ | 498.5 | 499 | —0.1 | >2.0 | 90(0) | 92 | 78 | 78(—1) |
| $F^-$ | 0.01 | $NH_4F$ | 497.5 | 499 | —0.3 | >2.0 | | | | |
| $F^-$ | 0.1 | $NH_4F$ | 463 | 499 | —7.2 | 2.4 | | | | |
| $F^-$ | 0.2 | $NH_4F$ (in crucible) | 435.5 | 499.5 | —12.8 | 2.5 | | | | |
| $F^-$ | 0.6 | $NH_4F$ (in crucible) | 345.5 | 499.5 | —30.8 | 2.6 | | | | |
| $F^-$ | 1 | $NH_4F$ (in crucible) | 276.5 | 499.5 | —44.6 | 2.7 | 72(—2) | 76 | 70 | 72(0) |
| $F^-$ | 1 | $NH_4F$ (in glass bottle) | | | | | 654(31) | 943 | 1425 | 950(30) |
| $I^-$ | 5 | KI b3 | | | | | 542(329) | 208 | 143 | 129(11) |
| $I^-$ | 0.05 | KI (red) b6 | | | | | 109(2) | 108 | 100 | 92(2) |
| $MoO_4^{-2}$ | 1 | $Na_2MoO_4 \cdot 2H_2O$ | 495 | 499 | —0.8 | >4.0 | 219(15) | 213 | 169 | 127(—8) |
| $MoO_4^{-2}$ | 5 | $Na_2MoO_4 \cdot 2H_2O$ | 447.5 | 499 | —10.3 | 4.0 | | | | |
| $MoO_4^{-2}$ | 5 | $Na_2MoO_4 \cdot 2H_2O$ (red) | 497.5 | 497 | 0.1 | >4.7 | 90(—1) | 99 | 95 | 98(9) |
| $NO_3^-$ | 1 | $KNO_3$ | — 39 | 499 | —107.4 | 2.3 | >2000 | >2000 | 622 | 715 |
| $NO_3^-$ | 0.69 | $Bi(NO_3)_3 \cdot 5H_2O$ (red) | 493 | 488.5 | 0.9 | >3.8 | | | | |
| $PO_4^{-3}$ | 100 | $H_3PO_4$ | 494 | 499 | —1.0 | 6.0 | | | | |
| $PO_4^{-3}$ | 300 | $H_3PO_4$ | 461 | 499 | —7.6 | 5.9 | 86(—1) | 91 | 80 | 81(1) |
| $PO_4^{-3}$ | 500 | $H_3PO_4$ | 389.5 | 499 | —21.9 | 5.7 | | | | |
| $SO_4^{-2}$ | 138 | $LiSO_4 \cdot H_2O$ | 495 | 499 | —0.8 | >6.0 | 88(3) | 90 | 81 | 80(0) |
| $VO_3^-$ | 50 | $NH_4VO_3$ | | | | | 1224 | 208 | 375 | 553 |
| $VO_3^-$ | 50 | $NH_4VO_3$ without 1,1′-dianthrimide | | | | | 2000 | 49 | 5 | 5 |
| $VO_3^-$ | 50 | $NH_4VO_3$ without 1,1′-dianthrimide (red) | | | | | 12 | 107 | 482 | 766 |

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[p] Another boron standard solution was used.

[q] Measured with Unicam SP 600 spectrophotometer.

[r] Niobium and titanium metal were dissolved in 5% sulfuric and 5% tartaric acid. Tantalum metal was dissolved in hydrofluoric acid. After dissolution this acid was removed by evaporation with sulfuric acid.

[s] Measurements at wavelengths below 500 mμ indicated complex formation.

[t] Later investigations showed complex formation.

[u] Exact *pRI* data were calculated for all % difference values ≧ 3. For % difference values > 1 or < 3, the *pRI* data are given in parenthesis. For % difference values ≦ 1, the *pRI* data were calculated under the assumption that % difference was < 2.

## RESULTS AND DISCUSSION

In the present investigation two types of interference were considered, *viz.* the effect of the foreign ion on the recovery of a known amount of boron, and the effect of the foreign ion on the blank solution containing only 1,1′-dianthrimide. The interference $RI_a$ of the foreign ion $a$ on the recovery of boron was defined as follows:

$$RI_a = \frac{(E_{a,b} - E_a) - (E_b - E_0)}{a} \Big/ \frac{E_b - E_0}{b}$$

and the interference $BI_a$ of the same ion on the blank solution was:

$$BI_a = \frac{E_a - E_0}{a} \Big/ \frac{E_b - E_0}{b}$$

In these expressions:
$a$ = concentration in p.p.m. of $a$ in the sample solution
$b$ = concentration in p.p.m. of boron in the sample solution
$E_0$ = extinction at 630 mμ of the blank solution
$E_a$ = extinction at 630 mμ of the sample solution containing $a$
$E_b$ = extinction at 630 mμ of the sample solution containing boron
$E_{a,b}$ = extinction at 630 mμ of the sample solution containing $a$ and boron

In Table I the interfering effect of the separate foreign ions on the recovery of a known amount of boron is given in the column headed $pRI$, where $pRI = -{}^{10}\log RI$. Thus, when the foreign ion $a$ and boron are present in equal weight concentrations, $pRI_a = 0$ indicates that both ions produce the same extinction with 1,1′-dianthrimide. At *e.g.* $pRI_a = 3$ the extinction of the boron solution is 1000 times higher than for the same weight concentration of the foreign ion $a$. The expressions introduced above have some useful properties. $BI$ can be expected to be approximately constant independent of the weight concentrations of $a$ and $b$, because $E_a - E_0$ for many ions is proportional to the weight concentration of $a$.

$$(E_{a,b} - E_a) - (E_b - E_a)/ab$$

was also found to be approximately constant, and consequently also

$$\frac{(E_{a,b} - E_b) - (E_a - E_0)}{ab} \cdot \frac{b}{E_b - E_0} = RI/b$$

When $RI_{a'}$ and $BI_{a'}$ were determined for the weight concentrations $a'$ and $b'$, and assuming that $RI_{a'}/b'$ and $BI_{a'}$ were independent of the concentrations of $a$ and $b$, then the relative error was:

$$\Delta b/b = a(RI_{a'}/b' + BI_{a'}/b)$$

The extinctions measured for the series of blank solutions are seen (Table I) to vary considerably. These variations were not always caused by the foreign ion, but could also originate from traces of boron present as impurities in the reagents. Thus, the addition of 0.1 g of a substance containing 0.1 p.p.m. of boron could be expected to increase the blank extinction by 0.005. By measuring the extinction of the blank solutions at different wavelengths, it was possible to draw conclusions whether any variations were caused by the formation of the boron 1,1′-dianthrimide complex or were due to a complex being formed between the foreign ion and the reagent.

In Table I the average extinctions of solutions without boron and foreign ion and prepared in glass bottle $b_1$ were 0.081, 0.085, 0.077 and 0.078 at the wavelengths 500, 570, 630 and 670 m$\mu$, respectively. (Some blank solutions were prepared in the glass bottles $b_2$, $b_3$, $b_4$, $b_5$ and $b_6$ and in these cases special corrections were used).

The differences of extinction between the blank solutions and the data for bottle $b_1$ given above were designated $\Delta E_{500}$, $\Delta E_{570}$, $\Delta E_{630}$ and $\Delta E_{670}$. If these differences were caused by boron, then (according to unpublished absorption data on the boron 1,1′-dianthrimide complex):

$$\Delta E_{500} - 0.412\ \Delta E_{630} = 0$$

$$\Delta E_{570} - 0.644\ \Delta E_{630} = 0$$

$$\Delta E_{670} - 0.624\ \Delta E_{630} = \Delta\Delta E_{670} = 0$$

The latter difference ($\Delta\Delta E_{670}$) is given in parenthesis in the column headed 670 m$\mu$ (Table I). High values for the first two differences were obtained for cadmium(II), aluminium(III), iron(III), magnesium(II), manganese(II) and ammonium persulphate. In these cases the decomposition of 1,1′-dianthrimide might have gone farther than normal, and in that case the decomposition products would increase the extinctions at the two lower wavelengths, 500 and 570 m$\mu$. If the variations of the extinction of the blank solutions were caused by the decomposition of the reagent, then (according to unpublished results on the decomposition of 1,1′-dianthrimide):

$$\Delta E_{500} - 0.412\ \Delta E_{630} - \frac{0.280}{0.226}\ (\Delta E_{570} - 0.644\ \Delta E_{630}) = 0$$

$$\text{or, } \Delta E_{500} - 1.24\ \Delta E_{570} - 0.387\ \Delta E_{630} = \Delta\Delta E_{500} = 0$$

The $\Delta\Delta E_{500}$ data are given in parenthesis in the column headed 500 m$\mu$ (Table I). It appeared from Table I that the majority of the ions examined had $\Delta\Delta E_{500}$ and $\Delta\Delta E_{670}$ values within the range $\pm 0.004$, and these ions therefore probably did not form complexes which absorb at the wavelengths employed.

The ions cobalt(II), nickel(II), copper(II) and chromium(III) are coloured in sulfuric acid, and sample solutions containing these ions gave high extinctions. By measuring solutions of these metals also in the absence of 1,1′-dianthrimide it was confirmed that their interfering effect originated from the colour of the ions. The data in Table I further indicate that germanium(IV) and tellurium (IV) formed complexes with 1,1′-dianthrimide. Later investigations have confirmed this and have shown that selenium(IV) also forms a complex with the reagent. The complexes with germanium, tellurium and selenium showed absorption curves in the same region as the boron 1,1′-dianthrimide complex. There was also found evidence of complex formation with zinc(II), but this complex showed negligible extinction at the wavelength of the absorption maximum of the boron complex (630 m$\mu$). (The application of 1,1′-dianthrimide for spectrophotometric determination of germanium[19], tellurium[20] and selenium[21] has been described).

According to MARTIN[22] germanium(IV) also interferes in the analysis of boron with chromotrope 2B. This author added hydroxylamine hydrochloride to avoid the interference. It is seen from Table I that the addition of hydrazine sulphate did not remove the interference from germanium and tellurium. Hydroxylamine hydrochloride was then tried and was found to be effective. The interference caused by complex formation of germanium(IV) and tellurium(IV) with 1,1′-dianthrimide can thus be removed by reduction with hydroxylamine hydrochloride.

Of the anions examined, the following interfered: bromide, iodide, fluoride, nitrate, orthophospate (in higher concentrations), vanadate and molybdate. The presence of bromide and iodide increased the extinctions of the sample and the blank solutions. Bromine and iodine were formed and it proved to be difficult to reduce these substances in sulfuric acid solution by the addition of hydrazine sulphate.

Fluoride ions had a marked influence on the recovery of boron, the effect increasing with the amount of fluoride added. The low results obtained in these cases were probably due to complex formation between boron and fluoride. The presence of fluoride further increased the extinction of the blank solutions considerably when glass bottles were applied. The data indicated formation of the boron 1,1′-dianthrimide complex. In these cases the glass was probably attacked by hydrofluoric acid and boron was brought into solution. On the other hand no increase of extinction was observed when blank solutions were heated in glazed porcelain crucibles.

Nitrate had a strong interfering effect on both the sample and blank solutions but this effect was completely removed by the preliminary reduction.

The recovery of boron was further influenced by higher concentrations of phosphate (added as phosphoric acid).

Molybdate was found to have an effect on the sample and blank solutions, but the interference was eliminated by reduction.

It was thus possible to remove the effect of many interfering ions by preliminary reduction with either hydroxylamine hydrochloride or hydrazine sulphate. When hydrazine sulphate was applied, the only ions interfering in the determination of boron with 1,1′-dianthrimide were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. The use of hydroxylamine hydrochloride removed the interference from germanium(IV) and tellurium(IV).

## ACKNOWLEDGEMENTS

The authors are indebted to Professor H. HARALDSEN for the facilities placed at their disposal, and to Professor J. LÅG (Agricultural College of Norway) who suggested this investigation.

## SUMMARY

The effects of about 40 inorganic ions and reducing and oxidizing agents on the determination of boron with 1,1′-dianthrimide were studied spectrophotometrically. The separate foreign ions were added both to solutions containing boron and 1,1′-dianthrimide and to solutions containing only 1,1′-dianthrimide. From the two series of extinction measurements conclusions were drawn as to the type of interference present. With the use of hydrazine sulphate as reducing agent, the only ions interfering were: germanium(IV), tellurium(IV), cobalt(II), nickel(II), copper(II), chromium(III), bromide, iodide, fluoride, vanadate and high concentrations of orthophosphate. A new method of indicating spectrophotometric interference was introduced.

## RÉSUMÉ

Les auteurs ont effectué une étude de l'influence des ions étrangers sur le dosage spectrophotométrique du bore au moyen de la dianthrimide-1,1′. Une nouvelle méthode est proposée avec traitement préalable à l'aide d'hydroxylamine ou d'hydrazine.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss von Fremd-Ionen, Oxydations- und

Reduktionsmittel auf die spektrophotometrische Bestimmung von Bor mit 1,1'-Dianthrimid. Die störende Wirkung einer Anzahl Fremdelemente kann durch Zusatz von Hydroxylamin oder Hydrazin ausgeschaltet werden.

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# SPECTROCHEMICAL DETERMINATION OF POTASSIUM IN GEOLOGICAL MATERIALS USING SPECTRAL LINE WIDTH

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(Received January 6th, 1961)

## INTRODUCTION

The method for the determination of the alkali elements in geological material (Shaw *et al.*[1]), using caesium as an internal standard and alkali elements lines in the range of 5700–8300 Å, suffers from one serious disadvantage. The three potassium lines in this region, K 6938, K 7664 and K 7698, show an intensity range insufficient to cover the range of concentration of potassium commonly found in rocks and minerals. K 7664 and K 7698 are suitable for very low potassium concentrations and K 6938 for relatively high amounts. Moreover, self-absorption is particularly noticeable in K 7664 and K 7698, seriously limiting the use of these lines in quantitative work.

A method utilizing line widths which are not affected by self-absorption or conditions of photographic development is described and the use of a line width-log intensity calibration curve is emphasized.

Line width as a measure of concentration was suggested by GERLACH AND ROLLWAGEN[2] and by EISENLOHR AND ALEXY[3] and was later used by BASTRON *et al.*[4]. Generally, a recording densitometer is used to scan the spectral line, and the line width of the analysis element is measured at a photographic response value or percent transmission reading equivalent to the maximum of the internal standard element. Emulsion calibration curves are not used and line widths are plotted directly against log concentrations to obtain the working curves.

## METHOD

The spectrochemical method is described in Table I and is essentially that of SHAW

TABLE I

SPECTROCHEMICAL METHOD

| | |
|---|---|
| *Spectrograph:* | Jarrell-Ash, 21 foot grating with Wadsworth Mount and 1st order dispersion of 5.2 A/mm. |
| *Slit:* | 11 mm × 30 u |
| *Intensity reduction:* | Rotating step-sector, log intensity ratio of 0.2 on adjacent steps, located at slit. Yellow filter. |
| *Exposure; and excitation:* | 60 sec at 5 A at 230 V with open circuit. In Stallwood air jet with air flow about 4 l/min. |
| *Photographic emulsion:* | Kodak type 1-N, used in range 5700-8300 Å, developed 4 min in D-19 developer at 20°. |
| *Electrodes:* | National Carbon Co. "special" grade, 1/8" dia. Anode has plain crater. |
| *Sample preparation:* | 1 part mineral with 1 part internal standard mix consisting of 50% $Cs_2CO_3$ in "special" grade graphite powder. |
| *Spectral lines:* | K 6938.980 Å<br>Cs 6983.488 Å (internal standard)<br>K 7664.907 Å<br>K 7698.979 Å |

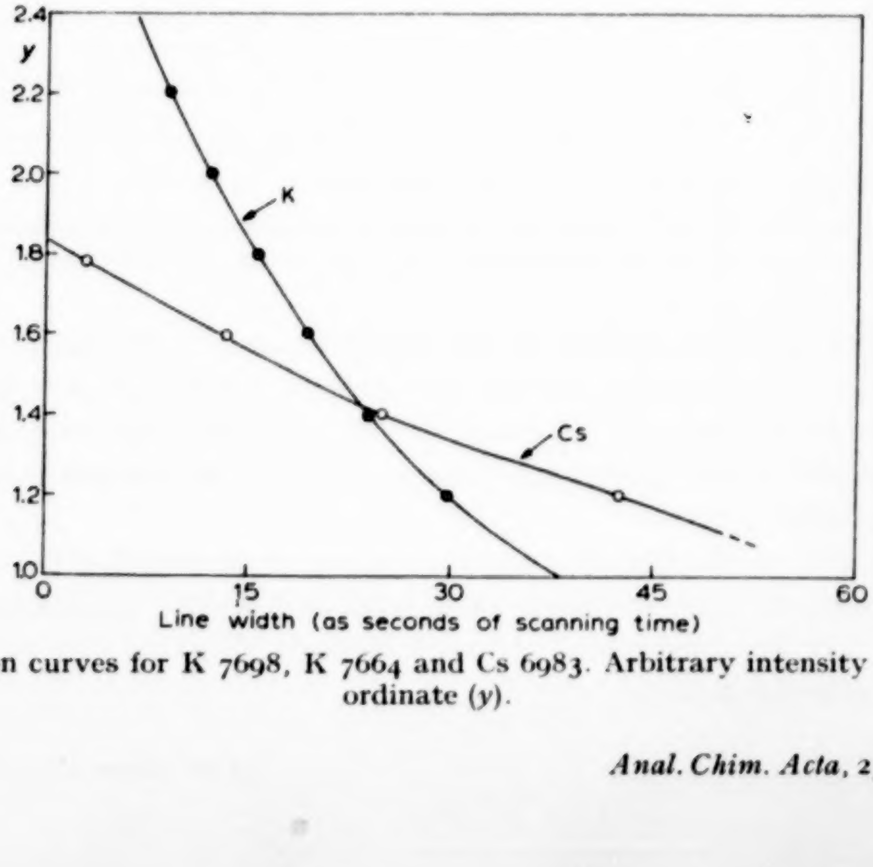

Fig. 1. Calibration curves for K 7698, K 7664 and Cs 6983. Arbitrary intensity values form the ordinate (*y*).

*et al.*[1], but a carbonate matrix is used. In the absence of a recording microdensitometer, line widths were obtained by recording the time interval required to scan the width of the spectral line so that percent transmission remained below some given value. A seven-step logarithmic step-sector was inserted at the slit and for K 7664, the time interval, during which the percent transmission remained below 50% on step 5, was measured, as was the interval when the percent transmission remained below 50 on step 3 of Cs 6983, the internal standard line. A direct plot of the K/Cs line width ratio against log concentration of K yielded a scatter diagram of no use as a working curve.

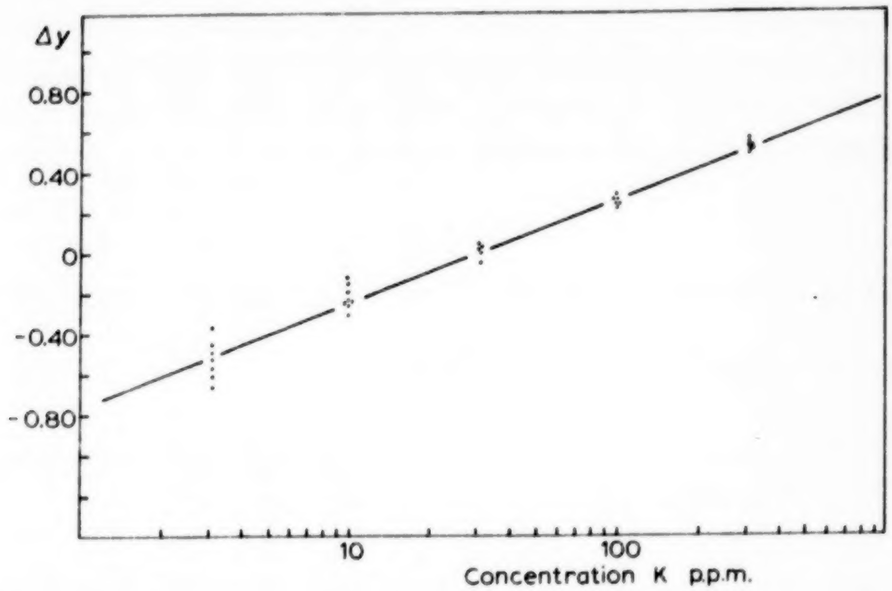

Fig. 2. Working curve for K 7664 constructed from line width measurements and drawn by linear regression. Log $I_{K/Cs}$ forms the ordinate ($\Delta y$).

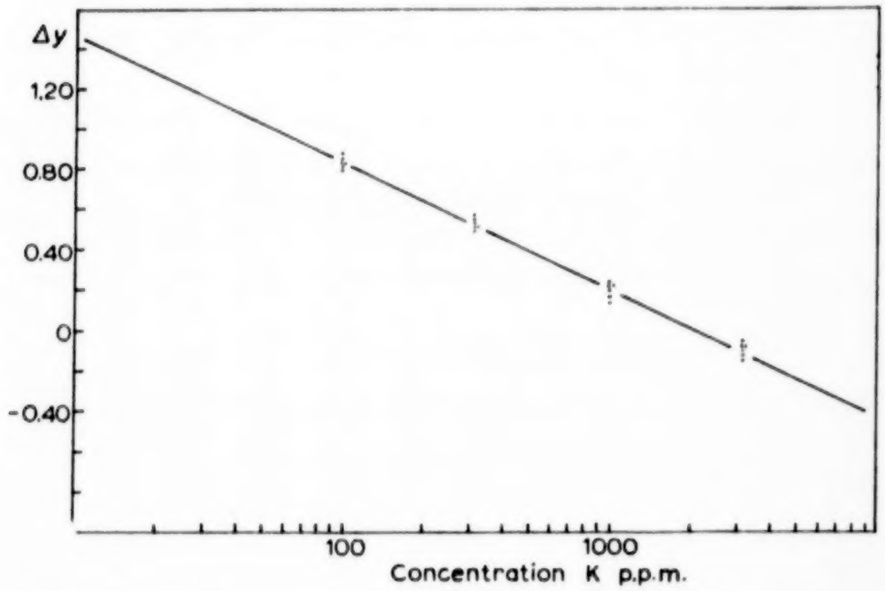

Fig. 3. Working curve for K 7664 constructed from line density (% transmission) measurements and drawn by linear regression. Log $I_{K/Cs}$ forms the ordinate ($\Delta y$).

By measurement of the line widths on adjacent steps which differ in intensity by log 0.2, a calibration curve relating log *I* with line width, measured in seconds of scanning time, can be constructed for each element (Fig. 1). The curves for K and for Cs differ markedly in slope.

A plot of log $I_{K/Cs}$ against log concentration yields the linear working curve shown in Fig. 2, the use of which permits extension of the working range of K 7664 far beyond the point of self-absorption until higher concentrations of potassium result in the appearance of K 6938. Besides bridging this important gap in potassium determination in a general method for alkalies, line width methods result in a considerably higher degree of reproducibility as shown by comparison with the working curve of Fig. 3 which was drawn using density measurements from the same set of plates. The success of the method is in part derived from the diffuse nature of the spectral lines in the 5700–8300 Å region. Density measurements on less intense lines such as Li 6707 and Rb 7800 may be carried out, of course, on the same plates as those used for line widths.

## ACKNOWLEDGEMENT

The writer is indebted to Imperial Oil Limited for funds to undertake a study of trace elements in carbonate rocks and to Prof. D. M. SHAW for kind permission to use his spectrographic facilities at McMaster University, Hamilton (Canada).

## SUMMARY

Line width, used as a measure of potassium concentration, is superior to spectral line density (or percent transmission) in a general DC arc spectrographic method for the determination of K in geological materials.

## RÉSUMÉ

Lors du dosage spectrographique du potassium dans les matériaux géologiques, les résultats les meilleurs ont été obtenus par mesure de la largeur des raies, et non par mesure de la densité des raies spectrales (% transmission).

## ZUSAMMENFASSUNG

Es wird gezeigt, dass bei der spektrographischen Bestimmung von Kalium in geologischen Materialien die Linienbreite ein besseres Kriterium für die Kaliumkonzentration ist als die Spektrallinienbichte (oder %-Transmission).

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# APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

## I. LEAD-BASE ALLOYS

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(Received October 1st, 1960)

In two earlier papers the author has described the application of controlled-potential electrolysis for the determination of some elements in the analysis of lead- and tin-base alloys.

Methods for the determination of copper in lead alloys and of copper and lead in tin-base alloys were given in the first paper[1]. Both methods use a 5-g sample because of the small amounts of copper present in lead alloys and of lead in tin alloys.

In a second paper[2] a method was described for the evaluation of lead in lead-base alloys and another method for the successive determination of lead and tin in lead- or tin-base solder alloys. Further investigations have permitted an improvement of this second method and a change in the analytical procedure whereby the volumetric determination of antimony is done before the electrolytic determination of lead. As a result, it is now possible to describe a combination of volumetric and controlled potential electrolytic methods which make possible the determination of the main elements in these alloys — copper, lead, tin and antimony — in a shorter time and, generally, more accurately than by conventional methods. For the alloys considered here, the main constituent elements — especially lead, tin and antimony — have percentages that vary within very wide limits. This paper deals in particular with those alloys which are more frequently analysed in our Laboratory and which have an antimony content of less than 10%; however, alloys with higher percentages of antimony may also be analysed on a weighed sample of 0.5 g. The elements interfering with the determinations described are silver and bismuth, which co-deposit with copper, and arsenic, which is titrated with antimony. Generally, these elements are present only in traces and, in the case of routine analyses for which these methods were devised, they have practically no effect on the results; for highly accurate analyses or when present in high percentages, these elements must be determined by appropriate methods[3].

The pH values mentioned later may be checked using narrow-range test papers, provided that the colour of these papers at the pH of the solution considered is checked, once and for all, with a pH-meter. For pH corrections during electrodepositions, the use of narrow-range test papers is essential.

Electrolyses were performed on an automatic control apparatus; platinum-gauze electrodes of height 50 mm and diameter 35 and 53 mm were used as anode and cathode, respectively. Current intensities mentioned later in the text refer to these types of electrodes; different sizes of electrodes may call for different current intensities.

## METHODS OF ANALYSIS

### *Determination of copper*

This may be performed by the method described in an earlier paper[1] either by a single electrolysis if antimony is less than 1.5% or by two electrolyses if antimony is in excess of 1.5%. Silver and bismuth, if any, co-deposit with copper.

### *Determination of antimony*

In a 400-ml tall-form beaker place 1 g of alloy, add 2 g of potassium pyrosulfate and attack the metal with 15 ml of concentrated sulfuric acid. The alloy must be in the form of thin chips or powder. Heat on a Bunsen burner, at first moderately and then strongly until the sulfuric acid fumes rise to the upper section of the beaker and partly recondense on the walls from which sulphur and its compounds must be eliminated. Next, continue the heating with a weaker flame or on a sand bath until the volume of the liquid is reduced to 5–6 ml. Allow to cool without covering the beaker. Into a graduated cylinder pour 15 ml of 1 : 1 hydrochloric acid and 10 ml of distilled water and cautiously transfer the solution obtained into the beaker, then stir. Dilute with 75 ml of distilled water, boil for 5 min while stirring with a glass rod, wash the rod with distilled water and allow to cool to about 50°.

Add 3–4 drops of an aqueous 1% methyl orange solution and stir the liquid and the precipitate constantly by magnetic stirring: titrate slowly with a potassium bromate solution to discouloration. Add two more drops of methyl orange solution and if the solution retains its colour proceed with the titration until discolouration is attained. The presence of lead sulfate precipitate does not interfere with the titration.

The bromate solution must be standardized against an alloy whose antimony content is known. Since antimony has to be titrated in both low and high percentages, it is advisable to have two different solutions, for instance, 0.025 *N* bromate for less than 3% antimony and 0.05 *N* bromate for higher amounts.

After titration, an excess of bromate is added: 2 ml of a solution about 0.05 *N* or the approximate equivalent of a solution of different normality.

Titration may also be done with potassium permanganate, standardized with a sample alloy, but much care must be exercised at the end-point because the solution changes from pink to colourless and then to pink again with the first drop of excess permanganate. Bromate titration should preferably be used.

The titration described is not correct if arsenic is present since arsenic is titrated as antimony. Generally, arsenic is present in very small quantities and in the bromate titration it is all, or nearly all, accounted as antimony; moreover, if arsenic exceeds 2–3 mg most of it will volatilize while the solution boils.

### *Determination of lead*

*(A) Antimony less than 3%.* To the solution in which antimony was determined, add 8 g of tartaric acid, 2 g of succinic acid, 1 g of hydrazine dihydrochloride and then

concentrated ammonia up to a pH of 7.2–7.3. The addition of ammonia, which may be done with a Ranvier bottle, serves to solubilize the lead sulfate. If necessary, adjust the pH to 7.2–7.3 by ammonia and 1 : 1 hydrochloric acid. Deposit lead on the previously copper-plated cathode. The cathode potential required to electrolyze lead is —0.65 V *vs.* S.C.E. but, initially, the potential is kept at a less negative value so as to obtain an initial intensity of 0.3–0.5 A; as electrolysis progresses and current intensity decreases, increase the cathode potential gradually to —0.65 V *vs.* S.C.E. When current intensity is reduced to 0.03–0.01 A, adjust the solution pH to about 5, without stopping the electrolysis. To correct the pH, add 1 : 1 hydrochloric acid from a Ranvier bottle. Wait until the intensity drops to a constant minimum value and, after 10–15 min, wash in the usual manner[4,5], dry and weigh.

Copper, silver and bismuth, the determination of which was already described, co-deposit with lead and must be subtracted from the percentage of lead found.

*(B) Antimony greater than 3%*. To the solution in which antimony was determined, add 8 g of tartaric acid and 2 g of succinic acid, followed by concentrated ammonia until lead sulfate is completely dissolved. If copper is present, the solution takes on a blue colouration. The pH required in this case may be even greater than 8, but addition of ammonia in excess must be avoided: when solubilization is nearly complete, add the ammonia in small amounts.

Neutralization by ammonia causes a heating of the solution. Cool below 35° and add, little by little, 1 g of hydrazine dihydrochloride: this addition does not affect appreciably the pH and, if carried out in small amounts, it will not cause re-precipitation of the lead sulfate. Copper is reduced by hydrazine and the solution becomes decolourized. The electrodeposition of lead begins at a cathode potential (generally in the —0.60 to —0.65 V *vs.* S.C.E. range) which corresponds to a current intensity of 0.3–0.5 A. After 15–20 min, and without stopping the electrolysis, adjust the pH of the solution to 7.2–7.3 with 1 : 1 hydrochloric acid and, if the current intensity increases, adjust the cathode potential to a less negative value (generally included in the —0.57 to —0.60 V *vs.* S.C.E. range) so that the current intensity does not exceed 0.3–0.4 A. There is no danger of re-precipitation of lead sulfate during pH correction as most of the lead was deposited during the initial 15–20 min. Electrolysis is then continued as described for (*A*) above.

Again the percentages of copper, silver and bismuth, must be subtracted from the percentage of lead. The arsenic present in the ammonia solution forms lead arsenate which becomes soluble — depending on the quantity present — at a pH of 7.2 to 8.5; lead will then deposit following either process (*A*) or (*B*) depending on the initial pH of the solution.

### *Determination of tin (antimony less than 3%)*

Antimony interferes with the electrodeposition of tin since it co-deposits if present in amounts greater than 3%. In this case, it is therefore preferable to titrate tin by the conventional iodimetric method, whereas, when the tin percentage is high and antimony does not exceeed 3%, the method described below gives more accurate results.

To deposit tin, add 30 ml of concentrated hydrochloric acid and about 0.2 g of hydrazine dihydrochloride to the solution from which lead was deposited and then electrolyze at —0.45 V *vs.* S.C.E.: a strong development of gas occurs and current intensity is very high — even greater than 1 A — but in a few minutes it drops to less than 0.1 A while gas formation decreases and then almost ceases. The cathode potential is then brought to —0.65 V *vs.* S.C.E.; however, if at this potential the initial current intensity is greater than 1 A, first electrolyze the solution at a less negative cathode potential so that the current intensity is not greater than 1 A and then, during electrolysis, increase the potential to —0.65 V *vs.* S.C.E.

Deposition of tin, towards the end, is rather slow and terminates when the intensity falls to a minimum constant value which, generally, lies in the 0.06- to 0.03-A range. Wait for 10–15 min, then wash, dry and weigh in the usual manner. Alloys containing less than 3% antimony are generally solders — numerous types of which exist — having as base metal both lead and tin. Provided that antimony is less than 3%, lead and tin may be determined by the methods described without any influence from the type of base metal (lead or tin), as shown in Table I.

A method for the electrolytic determination of tin even in the presence of more than 3% antimony will be described in the second part of this paper: this method was devised for tin-base alloys but is equally applicable to lead-base alloys.

## RESULTS

The methods described were used to analyse some synthetic solutions obtained from pure metal powders or thin chips and some standard samples. The synthetic solutions were prepared by dissolving antimony, lead and tin in the manner outlined above; copper was dissolved in nitric acid and then brought to white fumes with sulfuric acid. The two solutions obtained were then mixed. Table I gives the results obtained from the analysis of some synthetic solutions in which antimony amounts in all cases to less than 30 mg (3% on 1 g of weighed sample). Results are satisfactory also when lead or tin are prevalent.

TABLE I

ANALYSIS OF SYNTHETIC SOLUTIONS

| *No.* | *Sb* | | *Cu* | *Pb* | *Cu + Pb* | *Sn* | |
|---|---|---|---|---|---|---|---|
| | *Weighed* g | *Found* g | *Weighed* g | *Weighed* g | *Found* g | *Weighed* g | *Found* g |
| 1 | 0.0222 | 0.0223 | — | 0.8030 | 0.8035 | 0.2024 | 0.2019 |
| 2 | 0.0271 | 0.0275 | — | 0.8052 | 0.8047 | 0.2028 | 0.2033 |
| 3 | 0.0231 | 0.0232 | — | 0.6014 | 0.6019 | 0.4027 | 0.4027 |
| 4 | 0.0207 | 0.0210 | 0.0556 | 0.4890 | 0.5446 | 0.4538 | 0.4538 |
| 5 | 0.0218 | 0.0221 | 0.0333 | 0.4064 | 0.4396 | 0.5538 | 0.5542 |
| 6 | 0.0222 | 0.0226 | — | 0.2047 | 0.2045 | 0.7816 | 0.7811 |
| 7 | 0.0231 | 0.0233 | — | 0.8008 | 0.8004 | 0.2006 | 0.1999 |
| 8 | 0.0218 | 0.0222 | — | 0.6027 | 0.6022 | 0.4022 | 0.4018 |
| 9 | 0.0296 | 0.0300 | 0.0646 | 0.4822 | 0.5468 | 0.4512 | 0.4512 |
| 10 | 0.0243 | 0.0246 | 0.0307 | 0.4016 | 0.4320 | 0.5531 | 0.5531 |
| 11 | 0.0216 | 0.0218 | — | 0.2048 | 0.2045 | 0.7847 | 0.7850 |
| 12 | 0.0305 | 0.0308 | — | 0.2044 | 0.2039 | 0.7874 | 0.7870 |

Table II gives the results of some tests run in the presence of arsenic. For these tests the pH required for dissolution of the lead arsenate was from 8 to 8.5, depending on the amount present, and lead was therefore deposited according to method (*B*). From the results it may be inferred that: (*1*) some arsenic volatilizes while the solution is heated before titration by bromate; this is why the arsenic found is less than the amounts weighed; (*2*) arsenic does not interfere with the lead determination and (*3*) arsenic does not allow complete deposition of tin.

TABLE II

RESULTS OF THE DETERMINATIONS IN THE PRESENCE OF ARSENIC

| *No.* | *As* | | *Pb* | | *Sn* | |
|---|---|---|---|---|---|---|
| | *Weighed* g | *Found* g | *Weighed* g | *Found* g | *Weighed* g | *Found* g |
| 1 | 0.0060 | 0.0052 | 0.5170 | 0.5163 | — | 0.0002 |
| 2 | 0.0103 | 0.0071 | 0.4960 | 0.4962 | — | 0.0000 |
| 3 | 0.0202 | 0.0107 | 0.5024 | 0.5020 | 0.7006 | 0.6940 |
| 4 | 0.0050 | 0.0038 | 0.5141 | 0.5137 | 0.6895 | 0.6834 |
| 5 | 0.0116 | 0.0085 | 0.4022 | 0.4022 | 0.5977 | 0.5927 |
| 6 | 0.0226 | 0.0110 | 0.6037 | 0.6034 | 0.3982 | 0.3960 |
| 7 | 0.0212 | 0.0153 | 0.4014 | 0.4011 | 0.5945 | 0.5935 |
| 8 | 0.0107 | 0.0100 | 0.6033 | 0.6036 | 0.4442 | 0.4431 |
| 9 | 0.0105 | 0.0101 | 0.4022 | 0.4019 | 0.6247 | 0.6233 |
| 10 | 0.0219 | 0.0097 | 0.5997 | 0.5999 | 0.4294 | 0.4262 |

TABLE III

DETERMINATIONS ON SOLDER 127a (N.B.S.)

Composition: Pb 69.005%, Cu 0.004%, Bi 0.036%, Ag 0.004%, Sb 0.79%, As 0.129%, Sn 30.03%, Ni 0.002%, Pb + Cu + Bi + Ag = 69.049%

| *Test No.* | *Weighed (g)* | | | *Found (g)* | | | |
|---|---|---|---|---|---|---|---|
| | *Solder 127a* | *Sb* | *As* | *Sb (+ As as Sb)* | | *Pb* | *Sn* |
| | | | | *Theoret.* | *Found* | *(+Cu+Bi+Ag)* | |
| 1 | 1.0000 | — | — | 0.0100 | 0.0098 | 0.6909 | 0.3005 |
| 2 | 1.0000 | — | — | 0.0100 | 0.0097 | 0.6908 | 0.3002 |
| 3 | 1.0000 | — | — | 0.0100 | 0.0095 | 0.6911 | 0.2999 |
| 4 | 1.0000 | — | — | 0.0100 | 0.0096 | 0.6908 | 0.3005 |
| 5 | 1.0000 | 0.0200 | — | 0.0300 | 0.0294 | 0.6909 | 0.3002 |
| 6 | 1.0000 | 0.0202 | — | 0.0302 | 0.0298 | 0.6910 | 0.3008 |
| 7 | 1.0000 | 0.0206 | — | 0.0306 | 0.0305 | 0.6906 | 0.3000 |
| 8 | 1.0000 | 0.0220 | — | 0.0320 | 0.0322 | 0.6907 | 0.3005 |
| 9 | 1.0000 | 0.0192 | 0.0203 | 0.0622 | 0.0352 | 0.6906 | 0.3001 |
| 10 | 1.0000 | — | 0.0103 | 0.0267 | 0.0160 | 0.6907 | 0.3000 |

Table III summarizes the results obtained by analysing N.B.S. sample No. 127a. In some tests antimony was added and in others also arsenic. The amount of arsenic present was calculated as antimony after multiplication by the ratio of the two atomic weights. The sum of arsenic and antimony found was always lower than the theoretical value owing to the loss of a part of arsenic. Lead electrolysis was performed according to method (*A*) in tests 1 to 8 and method (*B*) in tests 9 and 10. On the basis of the latter two tests it may be inferred that arsenic does not prevent the complete deposition of tin if antimony is also present; this deduction is confirmed by the data given in Table IV which shows the good results obtained, not only in the electrodeposition of lead but also of tin; the sum of antimony and arsenic is again less than the theoretical amount.

The loss of arsenic could perhaps be avoided by adding 15 ml of 1 : 1 hydrochloric acid after boiling, instead of before as mentioned in the method described, but knowing exactly the sum of arsenic and antimony — estimated all as antimony — is of little interest; when the percentage of arsenic present is rather high both elements must be determined by separate methods[3]. In the present investigation only the influence of small amounts of arsenic on the electrolysis of lead and tin was examined and it may be concluded that arsenic is not an interfering factor, so long as antimony is also present.

TABLE IV

RESULTS OF THE DETERMINATIONS IN THE PRESENCE OF ARSENIC AND ANTIMONY

| *No.* | *As Weighed g* | *Sb Weighed g* | *Sb (+ As as Sb)* | | *Pb* | | *Sn* | |
|---|---|---|---|---|---|---|---|---|
| | | | *Theoret. g* | *Found g* | *Weighed g* | *Found g* | *Weighed g* | *Found g* |
| 1 | 0.0101 | 0.0311 | 0.0475 | 0.0421 | 0.4503 | 0.4500 | 0.3849 | 0.3850 |
| 2 | 0.0205 | 0.0308 | 0.0641 | 0.0470 | 0.4530 | 0.4528 | 0.6217 | 0.6211 |

TABLE V

LEAD-BASE ALLOYS WITH MORE THAN 3% ANTIMONY

| *Composition* | | *Weighed g* | *Method B* | | *Method A* | |
|---|---|---|---|---|---|---|
| | | | *Sb* | *Pb (+ Cu + Bi + Ag)* | *Sb* | *Pb (+ Cu + Bi + Ag)* |
| *53 d-Lead-base bearing metal (N.B.S.)* | | 1 | 9.95 | 85.02 | 9.98 | 85.24 |
| | | 1 | 9.98 | 85.06 | 9.91 | 85.22 |
| Pb = 84.69 | Sb = 9.92 | 1 | 9.88 | 85.02 | 10.01 | 85.22 |
| Cu = 0.268 | As = 0.045 | 1 | 9.87 | 85.10 | 9.96 | 85.22 |
| Bi = 0.135 | Sn = 4.94 | 1 | 9.93 | 85.04 | 9.97 | 85.24 |
| | Ni = 0.002 | 0.5 | 9.93 | 85.02 | 9.97 | 85.18 |
| | | 0.5 | 9.94 | 85.06 | — | — |
| *177/1 Lead-base white metal (B.C.S.)* | | | | | | |
| Pb = 84.5 | Sn = 5.09 | 1 | 10.36 | 84.45 | 10.37 | 84.59 |
| Cu = 0.007 | As = 0.005 | 1 | 10.36 | 84.51 | 10.37 | 84.62 |
| Bi = 0.002 | Fe = 0.004 | 0.5 | 10.39 | 84.56 | 10.33 | 84.54 |
| Sb = 10.42 | Zn = 0.01 | 0.5 | 10.35 | 84.50 | 10.38 | 84.55 |
| Sb = 7 | Pb = 93 | 1 | 7.05 | 92.93 | — | — |
| | | 1 | 6.96 | 93.01 | | |
| | | 1 | 7.01 | 92.94 | | |
| | | 1 | 6.97 | 92.96 | | |

The results of the determinations on two standard samples containing more than 3% of antimony and on a sample containing lead and antimony only are given in Table V. Tin was not determined electrolytically because there is partial co-deposition of antimony, hence the conventional iodimetric method is to be preferred.

Lead was deposited both by method (*B*) (hydrazine added in the cold after neutralization) and by method (*A*) (hydrazine added before neutralization): the Table shows that the latter method gives slightly high results and it was found that the cause for this is a co-deposition of some antimony, probably reduced by hydrazine in the solution heated by the neutralization with ammonia. Therefore, procedure (*B*) should be preferred if the antimony in the solution is more than 30 mg. Results which are practically identical and always satisfactory are obtained both with 0.5 and 1 g of weighed sample.

## ACKNOWLEDGEMENTS

Thanks are due to Dr. A. ZAZZARONI, Director of the FIAT Laboratories, and Dr. Ing. C. F. BONA, Director of FIAT's L.R.C.A.A., for kind permission to publish this paper, to Dr. S. BERTOLDI for stimulating discussions and to Mr. P. GIACCONE for his constructive cooperation.

## SUMMARY

The application of controlled-potential electrolysis to the determination of copper, lead and tin, after titration of antimony, is discussed for the analyses of lead-base and tin-base alloys.

## RÉSUMÉ

L'auteur a effectué une étude sur l'application de l'électrolyse à potentiel contrôlé au dosage du cuivre, du plomb et de l'étain, après titrage de l'antimoine, dans le cas d'alliages à base de plomb et à base d'étain.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung der Elektrolyse mit kontrolliertem Potential zur Bestimmung von Kupfer, Blei und Zinn in Blei- und Zinnlegierungen. Antimon wird vor der Elektrolyse durch Titration bestimmt.

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# POLAROGRAPHY OF SOME PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

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(Received January 3rd, 1961)

Certain aldoximes, in particular 1-methylpyridinium derivatives, are known to possess the ability to reactivate phosphorylated cholinesterase by nucleophilic attack and thus function as potential nerve gas antidotes[1-3]. In view of the fact that the oxime is a reducible function, it was of interest to study the polarography of such compounds in order to evaluate this method as an analytical technique for the determination of these oximes as well as to obtain information which might prove useful in interpreting the effect of substituents on the nucleophilicity of the oxime group.

The polarography of both aliphatic and aromatic aldoximes and ketoximes has been the subject of previous investigations[4-6]. In this respect, GARDNER AND GEORGAIS[7] have made an extensive study of the influence of pH on the reduction of oximes. More recently, LUND[8] has conclusively established, by means of controlled potential reduction, that oximes are reduced to the corresponding amines, a process which involves the uptake of four electrons. As part of a polarographic study of the positional effect of various substituents on the pyridine nucleus, TIROUFLET AND LAVIRON[9] included aldoximino-substituents.

This report concerns a study of the comparative polarography of 2-, 3- and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides. The observation that the pH dependence of diffusion currents and half-wave potentials of these compounds followed a course different from that previously reported for other aldoximes prompted a more elaborate study than otherwise might have been indicated. Furthermore, a specific effect of maximum suppressors on the half-wave potentials of aldoximes which has not been previously noted in the literature is reported.

## EXPERIMENTAL

### *Apparatus*

A Sargent Model XXI Polarograph, conventional H-cells, and saturated calomel reference electrodes were used to obtain all polarographic data. When the dropping mercury electrode was operated under a pressure of 47.5 cm of mercury, the drop time was 2.67 sec in 0.5 *M* potassium nitrate under open circuit. The capillary constant, $m^{2/3}t^{1/6}$, was 2.52 mg$^{2/3}$·sec$^{-1/2}$. Solutions were deaerated with purified nitrogen and maintained at a temperature of 25 $\pm$ 0.1° in a water thermostat for all measurements. Applied potentials on the polarograph were set with the aid of a Beckman Model G pH meter; polarograms were scanned at a rate of 1.23 mV/sec.

The cell resistances were measured with an alternating current Wheatstone bridge and found to be on the order of 500 ohms. Measured half-wave potentials were corrected for the $iR$ drop in solution when significant (*ca.* 5 mV). Some alternating current polarograms were also recorded on a modification of the Sargent Model XXI Polarograph described by COHEN AND LORDI[10]. For this purpose, a 50 cycle, 15 mV r.m.s. applied alternating current voltage was employed. The Beckman Model N pH meter was used for pH measurements.

### *Reagents*

Reagent or U.S.P. grade chemicals were employed wherever possible. The buffer solutions used in this work were nitric acid, glycine, and acetate for the acid range, phosphate for the neutral range, and borate, carbonate and tetramethylammonium for the basic range. In each case the ionic strength of the buffer was adjusted to 0.5 by the addition of appropriate quantities of potassium nitrate. The maximum suppressors used were gelatin, 15-cPs methylcellulose, Pluronic F68 (a polyoxyethylene polyoxypropylene glycol, Wyandotte Chemicals Corp.), benzalkonium chloride, and dioctyl sodium sulfosuccinate. The oximes employed in this study had been recrystallized from aqueous alcoholic solutions and dried over $P_2O_5$. Their melting points agreed with those previously reported[2].

### *Measurement of dissociation constants*

The apparent dissociation constants ($pK_a'$) of the oximes as acids were measured by titration of 50-ml aliquots of 0.005 to 0.01 $M$ solutions of the oxime in 0.5 $M$ $KNO_3$ with 0.5 $N$ sodium hydroxide. The titrant, delivered from an Agla micrometer syringe, was added to a jacketed beaker thermostated at 25° and a Beckman Model G pH meter was used to measure pH. The apparent dissociation constants of the conjugate acids of the pyridine aldoximes were determined by a similar titration with 0.5 $N$ nitric acid. The method of calculation used has been described elsewhere[11]. Results are recorded in Table I.

TABLE I

HALF-WAVE POTENTIALS ($-E_{1/2}$ *vs.* S.C.E.) OF PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

| *Compound* | $pK_a'$ | *pH* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *0.8* | *2.5* | *4.6* | *6.4* | *8.4* | *9.9* | *11.2* | *12.2* |
| Pyridine-2-aldoxime (PYA-2) | 9.9<br>3.8[a] | 0.70 | 0.74 | 0.84 | 1.10 | 1.32 | 1.48 | [b] | 1.74 |
| Pyridine-3-aldoxime (PYA-3) | 10.1<br>4.1[a] | 0.73 | 0.95 | 0.98 | 1.28 | [b] | [b] | [b] | [b] |
| Pyridine-4-aldoxime (PYA-4) | 9.6<br>4.9[a] | 0.50 | 0.67 | 0.71 | 0.92 | 1.19 | 1.34 | 1.49 | 1.57 |
| 1-Methylpyridinium-2-aldoxime (PAM-2) | 8.0 | 0.62 | 0.70 | 0.71 | 0.81 | 0.95 | 1.07 | 1.14 | 1.19 |
| 1-Methylpyridinium-3-aldoxime (PAM-3) | 9.1 | 0.69 | 0.87 | 0.96 | 1.05 | 1.17 | 1.25 | 1.30 | (1.37)[c] |
| 1-Methylpyridinium-4-aldoxime (PAM-4) | 8.5 | 0.45 | 0.63 | 0.67 | 0.72 | 0.87 | 0.96 | 1.05 | 1.13 |

[a] Apparent dissociation constant of conjugate acid of pyridine nucleus
[b] Waves obscured by solution decomposition current
[c] Ill-defined wave

### *Influence of media and D.M.E. characteristics on the polarographic wave*

Large maxima were observed when polarograms were scanned in solutions whose pH was such that the oxime was present in the undissociated form. In such cases well-defined waves were obtainable if gelatin was added in concentrations on the order of 0.06%. Higher concentrations of gelatin (*ca.* 0.1%) appeared to have no significant effect on the wave. The maxima tended to disappear in more basic solutions. The addition of 20% alcohol to the buffered solutions also affected maximum suppression. Since it was desirable to obtain comparative polarographic data in aqueous media, however, waves were scanned in buffered solutions containing 0.06% gelatin and 1 m*M* oxime.

All compounds studied exhibited well-formed waves corresponding to the reduction of the azomethine group ($\rangle C{=}N-$). The measured half-wave potentials are recorded in Table I and representative values of the limiting current constants, $i_d/m^{2/3}t^{1/6}C$, are listed in Table II. In order to demonstrate more clearly the effect of pH on the half-wave potential, the data obtained for PAM-2 (see Table I) and PYA-2 are also shown in Fig. 1. Similar curves were obtained when data for the other two sets of compounds were plotted.

TABLE II

REPRESENTATIVE LIMITING CURRENT CONSTANTS, $i_d/m^{2/3}t^{1/6}C$[a], OF PYRIDINE AND 1-METHYLPYRIDINIUM ALDOXIMES

| *Compound* | *pH* | | | |
|---|---|---|---|---|
| | *0.8* | *4.6* | *8.4* | *12.2* |
| PYA-2 | 8.7 | 8.5 | 8.0 | (7.5)[b] |
| PYA-3 | 8.8 | 9.2 | [b] | [b] |
| PYA-4 | 8.9 | 8.9 | 8.7 | (7.3)[b] |
| PAM-2 | 9.0 | 8.7 | 8.8 | 8.3 |
| PAM-3 | 8.6 | 8.7 | 8.9 | (5.3)[c] |
| PAM-4 | 8.8 | 8.8 | 8.7 | 7.9 |

[a] µA mg$^{-2/3}$ sec$^{1/2}$ mmole$^{-1}$ values of droptimes were measured at the $E_{1/2}$ and $m$ was 3.13 mg sec$^{-1}$
[b] Waves obscured by solution decomposition potential
[c] Ill-defined wave

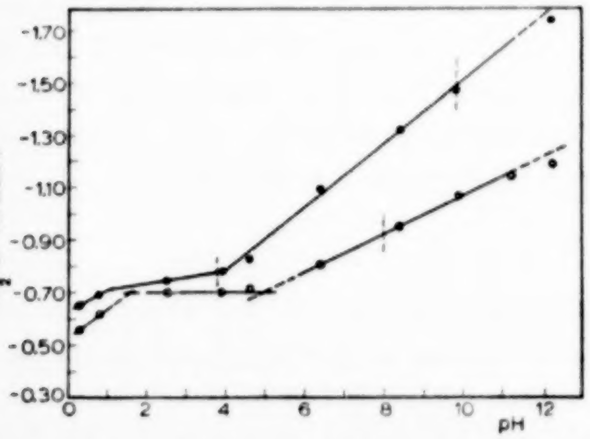

Fig. 1. Effect of pH on half-wave potentials (*vs.* S.C.E.) of pyridine-2-aldoxime (-○-○-○-) and 1-methylpyridinium-2-aldoxime (-●-●-●-), using 0.06% gelatin as maximum suppressor. Vertical dashed lines represent apparent dissociation constants of aldoximes.

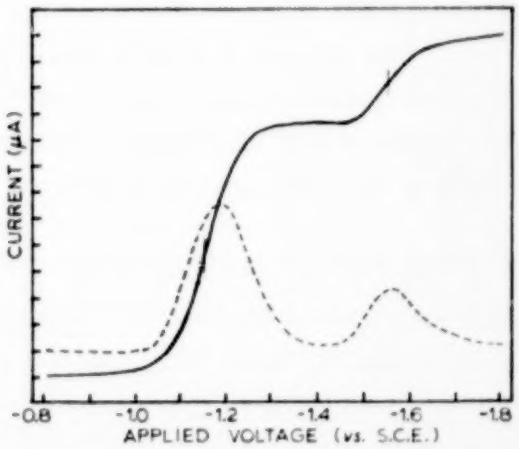

Fig. 2. Comparison of alternating current (– – – – – –) and direct current (———) polarograms scanned in carbonate buffer, pH 11.2, using 0.06% gelatin added as maximum suppressor. Arbitrary current scale.

Additional experiments were performed with PAM-2 and PYA-2, in order to characterize more fully the reduction of the aldoximes studied. Limiting currents were found to be linearly related to concentration from 0 to $2 \cdot 10^{-3}$ $M$. No significant changes in half-wave potential with variation of oxime concentration, buffer composition or buffer concentration were noted. In addition, when calcium chloride was used instead of potassium nitrate to adjust ionic strengths, no changes were observed in the waves. Since limiting currents were also found to be a linear function of the square root of the applied mercury pressure (corrected for the backpressure[12]), diffusion control was indicated over the entire pH range studied. In this respect the variation in half-wave potential, when the droptime was changed from 1.5 to 8.8 sec, amounted to no more than 0.02 V. Furthermore, waves which were scanned in reverse (negative to positive potential) were identical to those obtained by conventional scan (positive to negative potential).

The diffusion currents of waves scanned in media containing 20% alcohol were generally 20% lower than the currents of the waves scanned in aqueous media, while their half-wave potentials differed by no more than 0.02 V when gelatin was present. However, in the absence of gelatin, half-wave potentials of waves scanned in aqueous alcoholic media were on the order of 0.1 V less negative than those of waves scanned in aqueous media, except at pH $\sim$ 1 where the difference amounted to 0.2 V.

As a first approximation, the waves were symmetrical, as determined by the linearity of a plot of log $(i_d - i)/i$ *versus* applied potential. Values of $\alpha$[12] computed from the slopes of such plots were less than one.

At high pH values a second wave, which was obscured by hydrogen discharge in more acidic solutions, was observed in the case of the 1-methylpyridinium aldoximes. In the presence of gelatin the second wave was distorted and in its absence maxima were observed. Clearly defined, symmetrical waves were obtained for PAM-2 when 0.01% Pluronic F68 was used as a maximum suppressor in the trimethylammonium buffer of pH 12.2. The half-wave potential was $-1.53$ V and the limiting current about one-fifth that of the current due to the reduction of the aldoximino-group. The limiting current was diffusion controlled as indicated by the linearity of the plot of current *versus* square root of the mercury pressure. The half-wave potential of the second wave of PAM-4, measured under similar conditions, was $-1.62$ V. No satisfactory measurements of the second wave of PAM-3 could be made.

### *Alternating current polarographic studies*

Limited studies of the alternating current characteristics of the aldoximes were made in order to shed light on the nature of the electrode processes involved in the reduction. The following general observations were made on the basis of experiments with PAM-2 and PYA-2. Distorted peaks were obtained in aqueous media in the absence of maximum suppressor. Symmetrical peaks, with summit potentials 50–100 mV more negative than the corresponding half-wave potentials of the d.c. waves, were obtained when solutions containing alcohol or gelatin were scanned. At pH values where the d.c. polarogram of PAM-2 exhibited two waves, the a.c. polarogram also showed two peaks. A representative example is illustrated in Fig. 2, which shows a comparison of a d.c. and a.c. polarogram of PAM-2 measured at pH 11.2. No significance should be attached to the current scale which has been arbitrarily plotted.

### *Influence of maximum suppressors on polarographic waves*

The observation that measured half-wave potentials of the oximes studied differed when maximum suppressors other than gelatin were employed prompted a study of the effect of concentration and nature of maximum suppressor on the wave forms of PAM-2 and PYA-2. A representative example of the effect of concentration of maximum suppressor on wave form is shown in Fig. 3, in this case, the effect of 15 cPs methylcellulose on PAM-2. Diffusion currents were not altered significantly by the addition of maximum suppressor over the range of concentration studied (0 to 0.1%), but half-wave potentials were shifted to more negative values. In the specific case of methylcellulose, clearly defined waves were observed at concentrations ⩽ 0.01% and ⩾ 0.04%. Between 0.01% and 0.04% added methylcellulose, the waves observed were distorted and exhibited anomalies. At concentrations ⩾ 0.04%, the half-wave potentials were constant.

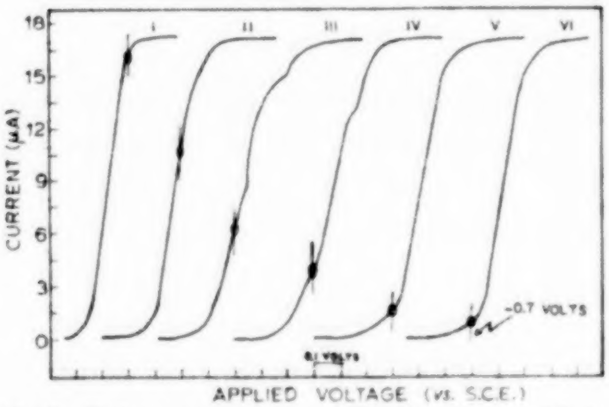

Fig. 3. Effect of 15-cPs methylcellulose on waves of PAM-2, $10^{-3}$ *M*, in acetate buffer containing 20% alcohol, pH 4.8. (I) 0%, (II) 0.01%, (III) 0.015%, (IV) 0.02%, (V) 0.04%, and (VI) 0.08% with respect to methylcellulose. Curves are displaced on abscissa scale. Vertical lines crossing waves represent −0.7 V.

TABLE III

COMPARISON OF MAXIMUM SUPPRESSOR EFFECTS ON HALF-WAVE POTENTIALS ($-E_{1/2}$ *vs.* S.C.E.) OF $10^{-3}$ *M* PYA-2 AND PAM-2 IN 20% ALCOHOLIC SOLUTIONS

| *Maximum suppressor* | *Concn.* % | *Aldoxime* | *pH*[a] | | |
|---|---|---|---|---|---|
| | | | *1.0* | *4.8* | *12.4* |
| None | — | PYA-2 | 0.52 | 0.76 | 1.69 |
| | | PAM-2 | 0.38 | 0.62 | 1.12 |
| Gelatin | 0.1 | PYA-2 | 0.70 | 0.89 | 1.73 |
| | | PAM-2 | 0.60 | 0.72 | 1.19 |
| Methylcellulose | 0.1 | PYA-2 | 0.84 | 0.98 | 1.78 |
| | | PAM-2 | 0.73 | 0.82 | 1.23 |
| Pluronic F68 | 0.1 | PYA-2 | 0.79 | 0.98 | 1.74 |
| | | PAM-2 | 0.77 | 0.88 | 1.23 |
| Benzalkonium chloride | 0.01 | PYA-2 | [b] | 0.96 | (1.80)[c] |
| | | PAM-2 | [b] | 0.86 | 1.22 |
| Dioctyl sodium sulfosuccinate | 0.02 | PYA-2 | 0.75 | 0.84 | [d] |
| | | PAM-2 | 0.68 | 0.83 | [d] |

[a] Measured pH values of aqueous alcoholic buffered solutions

[b] Benzalkonium chloride was incompatible with the acid buffer.

[c] Wave was obscured by a maximum.

[d] Dioctyl sodium sulfosuccinate was incompatible with the trimethylammonium buffer.

The data recorded in Table III show the effect of the nature of maximum suppressor on the half-wave potentials of PAM-2 and PYA-2. Measurements were made in aqueous alcoholic media in order to eliminate maxima. Gelatin and methylcellulose were examples of charged and uncharged hydrophilic colloids. Pluronic F68 is a nonionic surfactant, benzalkonium chloride a cationic surfactant, and dioctyl sodium sulfosuccinate an anionic surfactant. The maximum suppressors were used in concentrations necessary to insure constancy of half-wave potential.

## DISCUSSION

The observed order of ease of reduction of both the pyridine and 1-methylpyridinium aldoximes, *i.e.*, 4- > 2- > 3- substituted, is in agreement with the order which TIROUFLET AND LAVIRON[9] reported for other substituted pyridines. The ease of reduction of the PAM derivatives, as compared to the pyridine aldoximes, was to be expected because of the greater electron affinity of the quaternary group. The difference in half-wave potentials between the two groups of compounds is smallest (Fig. 1) at those pH values ($<5$) at which the electron affinity of the pyridine nitrogen is increased by protonation. This difference becomes increasingly greater as the pH is increased.

Unconjugated oximes are reported[5,8] to show a single pH dependent wave in acid solution, the height of which decreases at higher pH values and finally disappears in more basic solutions. The polarographic behaviour of the $\alpha,\beta$-unsaturated and aromatic oximes differ from that of the simple aliphatic oximes in that a second wave is observed at those pH values at which the first wave diminishes in height. GARDNER AND GEORGAIS[7] have presented a possible explanation for this phenomena. The height of the second wave increases until it is comparable in value to that of the first wave and then diminishes again at very high pH values. In contrast, a significant reduction in wave heights was observed in the case of the pyridine and 1-methylpyridinium aldoximes only at pH $> 10$. Statements have also been made to the effect that the oxime anion, $R{-}CH{=}N{-}O^-$, is not polarographically reducible[6]. In the particular cases studied, reduction waves were observed at pH values at which the aldoximes were present in the anionic forms.

The amines, which are products of the reduction of oximes, are not polarographically oxidizable[7], indicating that the overall electrode process involved in the reduction is irreversible. However, since well-defined alternating current polarograms were observed, the electrode process should more correctly be characterized as being "quasi-reversible". Reversible as well as irreversible electrochemical reactions must be involved in the electrode process. Totally irreversible processes could not be studied by alternating current polarography[13].

LUND[8] has suggested that the reduction of oximes involves reductive splitting of the N—O bond followed by saturation of the carbon-nitrogen double bond. Therefore, the mechanism of reduction of the aldoximes studied may be formulated as follows:

(*1*) In acidic solutions, pH $< 2$:

$$\begin{aligned}
&R{-}CH{=}NOH &&+ \ H^+ &&\rightarrow (R{-}CH{=}NOH)H^+\\
&+2e^- &&+ \ 2H^+ &&\rightarrow (R{-}CH{=}NH)H^+ + H_2O\\
&+2e^- &&+ \ 2H^+ &&\rightarrow R{-}CH_2{-}NH_3^+
\end{aligned}$$

(*2*) In neutral to alkaline solutions, pH $> 5 <$ p$K_a'$:

$$\begin{aligned} \mathrm{R{-}CH{=}NOH} + 2e^- + \mathrm{H_2O} &\rightarrow \mathrm{R{-}CH{=}NH} + 2\mathrm{OH}^- \\ + 2e^- + 2\mathrm{H_2O} &\rightarrow \mathrm{R{-}CH_2{-}NH_2} + 2\mathrm{OH}^- \end{aligned}$$

(*3*) In alkaline solutions, pH $>$ p$K_a'$:

$$\begin{aligned} \mathrm{R{-}CH{=}NO^-} + 2e^- + 2\mathrm{H_2O} &\rightarrow \mathrm{R{-}CH{=}NH} + 3\mathrm{OH}^- \\ + 2e^- + \mathrm{H_2O} &\rightarrow \mathrm{R{-}CH_2{-}NH_2} + 2\mathrm{OH}^- \end{aligned}$$

At pH values between 2 and 5 elements of both reaction pathways (*1*) and (*2*) probably occur simultaneously. In alkaline solutions an alternate reaction pathway which involves saturation of the carbon–nitrogen double bond preceding the reductive splitting of the N—O bond is likely. The intermediate would be a hydroxylamine, $\mathrm{R{-}CH_2{-}NHOH}$, instead of an imine. Since N-benzylhydroxylamine is reportedly[8] reduced at more positive potentials in alkaline solutions than is benzaldoxime, while in acidic solutions it is reduced at more negative potentials, this alternate pathway appears feasible. One must also account for the fact that reversible steps are involved in the electrode process. In this respect, further work involving a study of the mechanism of polarographic reduction of oximes is in progress.

The second wave observed in the case of the PAM derivatives probably corresponds to the reduction of the 2-aminomethyl-1-methylpyridinium iodide formed by reduction of the aldoxime. The mechanism of reduction may follow a course similar to that proposed for 1-methylpyridinium hydroxide[14].

The ability of maximum suppressors to shift the waves of the PAM derivatives and pyridine aldoximes to more negative potentials without altering diffusion currents is one of the possible effects of maximum suppressors on polarographic waves described by Meites and Meites[15]. Strassner and Delahay[16] have suggested that such effects result because of the ability of the maximum suppressor to alter the kinetics of the electrode reaction. The adsorption of a capillary-active substance at the mercury-solution interface would cause a decrease in the rate of the first electrochemical step, resulting in a more negative half-wave potential. One could infer from the fact that the observed half-wave potentials became constant that, after a critical bulk concentration of maximum suppressor had been reached, the interface had become saturated with respect to the maximum suppressor. Specific complex formation between the aldoxime and the maximum suppressor is not indicated, since diffusion currents were unaltered irrespective of the concentration and nature of the maximum suppressor. Furthermore, maximum suppressors of a wide variety of chemical type had qualitatively the same influence on the polarographic waves.

The polarographic method appears to be well suited to the determination of the oximes studied in the pH range 0 to 12; however, pyridine-3-aldoxime can only be determined in acidic solutions. Diffusion currents are proportional to concentration and are of large value (*e.g.*, 20 $\mu$A·mmole$^{-1}$), which should result in good sensitivity.

## ACKNOWLEDGEMENTS

The authors wish to thank Dr. Robert Ellin of the Physiological Chemistry Branch, U.S. Army Chemical Research and Development Laboratories, Army Chemical Center, Maryland for supplying the aldoximes used in this study, and Drs. Bartley J. Sciarrone and Thomas Medwick for discussions of this work.

## SUMMARY

The polarographic characteristics of 2-, 3-, and 4-aldoximino-substituted pyridines and 1-methylpyridinium iodides are reported. Well-defined, diffusion controlled, cathodic waves were observed, with the exception of pyridine-3-aldoxime, over the pH range 0–12 for the overall irreversible reduction of the oxime group to a primary amine, a process which involves the uptake of four electrons. The 1-methylpyridinium aldoximes were more easily reduced than were the corresponding pyridine aldoximes, particularly at high pH values where the pyridine nitrogen was unprotonated. Within each series the ease of reduction was as follows: 4- > 2- > 3-substituents. At high pH values a second cathodic wave was also observed in the case of the 1-methylpyridinium aldoximes which corresponded to reduction of the methylpyridinium nucleus. Alternating current polarographic studies indicated that the electrode process involved some reversible electrochemical steps. In addition, maximum suppressors were observed to shift half-wave potentials to more negative values without altering diffusion currents.

## RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement polarographique de quelques pyridine- et méthyl-1-pyridinium-aldoximes. Les vagues cathodiques obtenues sont généralement bien définies. Dans le cas des méthyl-1-pyridinium-aldoximes, on observe à des pH élevés une deuxième vague, correspondant à la réduction du noyau méthylpyridinium.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das polarographische Verhalten einiger Pyridin- und 1-Methylpyridin-aldoxime. Die beobachteten kathodischen Wellen sind gut definiert. Bei 1-Methylpyridin-aldoximen wird bei höheren pH Werten eine zweite Welle beobachtet, die durch die Reduktion des Methylpyridins verursacht wird.

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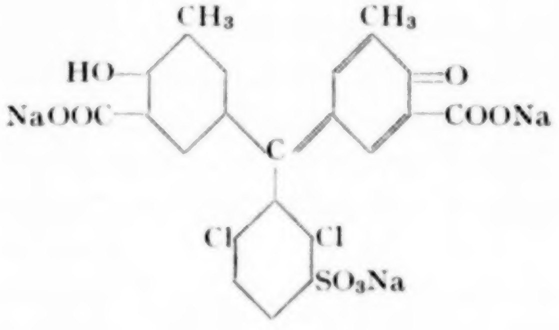
# Short Communications

## Dissoziationskonstanten von Chromazurol S

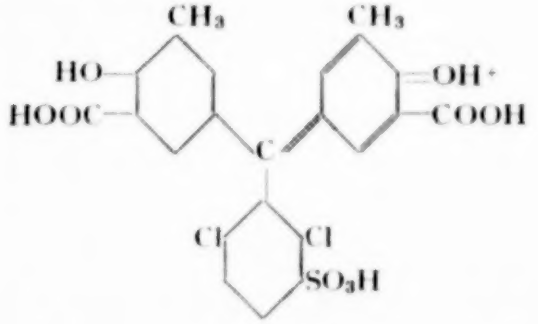
Chromazurol S (I) — Schultz-Lehman No. 841, Colour Index No. 723 — wird als chelatometrischer Indikator[1,2], sowie als kolorimetrisches Reagens[1] zur Bestimmung einer ganzen Reihe von Kationen benützt.



I

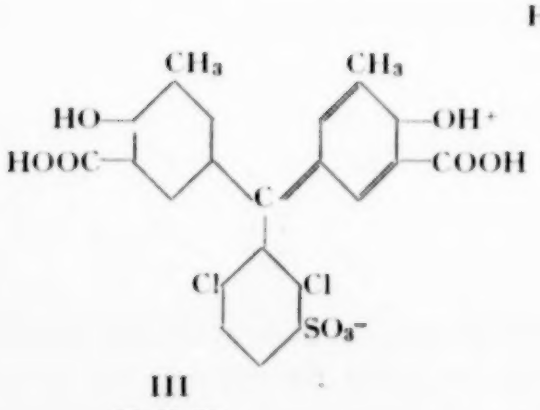
Seinen acidobasischen Eigenschaften nach können wir es zur Gruppe der Sulfonphtaleinindikatoren einreihen, die mehrere Farbumschläge sowie Farbumschläge in stark sauerem Medium aufweisen.

Die Farbwechsel von (I) mit steigendem pH der Lösung sind mit fortschreitender Ionisation des Farbstoffmoleküls verbunden, und seine Dissoziationsformen mit symmetrischem Resonanzsystem haben die tiefsten Farbtöne. In sauerem Medium (pH $\doteq$ 0) ist die Lösung von (I) orangefarben, die Farbe gehört dem Zwitterion $H_4ChS^\circ$(III). Durch Deprotonation des Zwitterions entsteht das Anion $H_3ChS^-$(IV) ($\lambda_{max}$ = 480 m$\mu$) von derselben Farbe. In stark sauerem Medium (>15 $N$ $H_2SO_4$) schlägt die Indikatorfarbe von orangefarbig nach rot um. Da unter diesen Bedingungen die Dissoziation der Sulfogruppe völlig herabgedrückt ist, setzen wir in der Lösung die An-



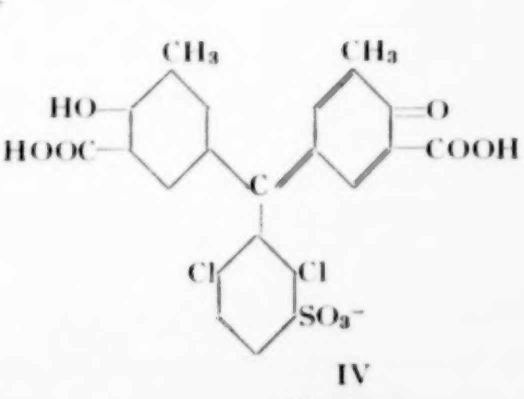
II

$H_5ChS^+$



III

$H_4ChS^\circ$



IV

$H_3ChS^-$

*Anal. Chim. Acta*, 25 (1961) 289–291

wesenheit des Kations $H_5ChS^+$(II) ($\lambda_{max}$ = 540 m$\mu$) voraus. Mit steigendem pH werden die Wasserstoffionen der beiden Karboxylgruppen ($H_2ChS^{-2}$, rote Farbe, $\lambda_{max}$ = 500 m$\mu$ und $HChS^{3-}$, gelbe Farbe, $\lambda_{max}$ = 430 m$\mu$) und endlich das Phenolwasserstoffion ($ChS^{4-}$, violette Farbe, $\lambda_{max}$ = 590 m$\mu$) stufenweise dissoziiert. Die Dissoziation des letztgenannten Wasserstoffions ist mit einem starken bathochromen und hyperchromen Effekt verbunden. Die Gleichgewichte von (I) in der normalen pH-Skala werden schematisch in der Gleichung (1) dargestellt, und es wurden auch die entsprechenden Dissoziationskonstanten errechnet. Die Absorptionskurven von (I) in stark sauerem Medium sind in Fig. 1, die Kurven die den anderen Gleichgewichtzuständen entsprechen in Fig. 2 dargestellt; die isosbestischen Punkte (458, 466 und 490 m$\mu$) beweisen das einfache Gleichgewicht zwischen den einzelnen Farbformen von (I).

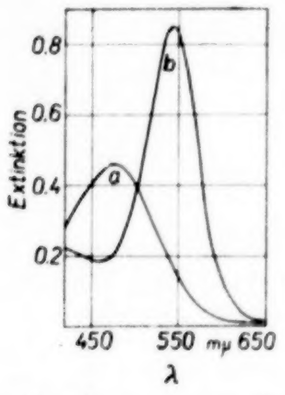


Fig. 1. Absorptionskurven von Chromazurol S in stark sauerem Medium; $c_{ChS} = 4 \cdot 10^{-5}$ $M$; Kurve *a*: $c_{H_2SO_4}$ = 0.83 $N$, Kurve *b*: $c_{H_2SO_4}$ = 14.23 $N$.

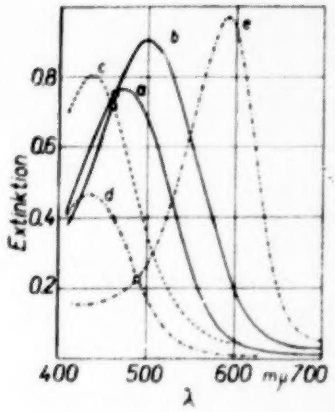


Fig. 2. Absorptionskurven von Chromazurol S; $H_3ChS^-$: Kurve *a* — pH = 1.14, $H_2ChS^{-2}$: Kurve *b* — pH = 3.02, $HChS^{-3}$: Kurve *c* — pH = 5.96, und *d* — pH = 8.44, $ChS^{-4}$: Kurve *e* — pH = 12.35; $c_{ChS} = 4 \cdot 10^{-5}$ $M$ (bei Kurven *d* und *e* nur $2 \cdot 10^{-5}$ $M$).

$$\begin{array}{ccccccc} & a & & b & & c & \\ H_3ChS^- & \rightleftharpoons & H_2ChS^{-2} & \rightleftharpoons & HChS^{-3} & \rightleftharpoons & ChS^{-4} \\ \text{orangefarben} & pK_1 & \text{rot} & pK_2 & \text{gelb} & pK_3 & \text{violett} \end{array} \qquad (1)$$

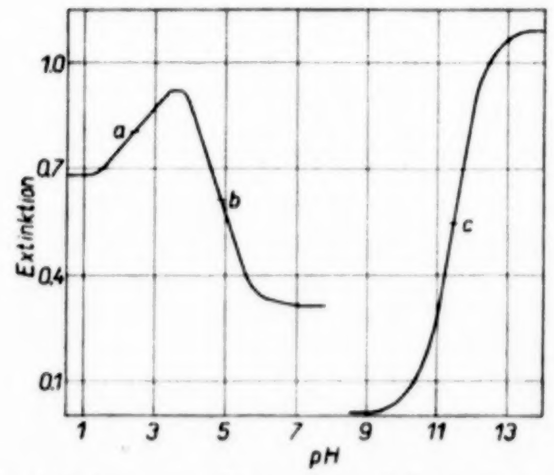


Fig. 3. Abhängigkeit der Extinktion von Chromazurol S vom pH-Wert; $c_{ChS} = 4 \cdot 10^{-5}$ $M$; $\lambda$: Kurven *a*, und *b* — 500 m$\mu$, Kurve *c* — 590 m$\mu$.

Die violetten und gelben Lösungen des Indikators sind beständig, die Farben im saueren Gebiet (rot, orangefarben) sind labil, und die Extinktion der Lösungen ändert sich schon nach 30 Min.

Die Dissoziationskonstanten von (I) wurden in normaler Weise[3,4] aus den Kurven $E = f(\text{pH})$ errechnet, die bei konstanter Indikatorkonzentration und bei dem Absorptionsmaximum einer der Farbformen (Fig. 3) gemessen wurden. Für jede Dissoziationskonstante gilt allgemein die Beziehung

$$K = \frac{[H^+]\,[H_{i-1}ChS^{i-5}]}{[H_iChS^{i-4}]} \qquad (2)$$

wo für die Gleichgewichtzustände *a*, *b* und *c* die Konstanten $K_1 (i = 3)$, resp. $K_2 (i = 2)$ und $K_3 (i = 1)$ gelten. Ferner gilt für jedes Gleichgewicht die Beziehung (3), welche die Gesamtkonzentration des Indikators und die Beziehung (4), die in jedem Punkte des aufsteigenden Abschnittes der Kurve gemessene Extinktion ausdrückt, wo $\varepsilon_i$ den molaren Extinktionskoeffizient der entsprechenden Partikel und *d* die Schichtdicke der gemessenen Lösung bedeutet.

$$c_{\text{ChS}} = [H_iChS^{i-4}] + [H_{i-1}ChS^{i-5}] \qquad (3)$$

$$E \cdot d^{-1} = \varepsilon_i [H_iChS^{i-4}] + \varepsilon_{i-1} [H_{i-1}ChS^{i-5}] \qquad (4)$$

Der Wert jeder Dissoziationskonstante ist durch Lösung der Gleichungen (2), (3) und (4) zu erhalten. So gelangt man zum allgemeinen Ausdruck für $K$

$$K = [H^+]\,\frac{E - \varepsilon_{i-1} \cdot d \cdot c}{\varepsilon_i \cdot d \cdot c - E} \qquad (5)$$

Die Werte der derart errechneten Dissoziationskonstanten und ihre negative Logarithmen sind in der Tabelle I zusammengefasst.

TABELLE I

DISSOZIATIONSKONSTANTEN VON CHROMAZUROL S

| | |
|---|---|
| $K_1 = 3.51 \cdot 10^{-3}$ | $pK_1 = 2.45$ |
| $K_2 = 1.38 \cdot 10^{-5}$ | $pK_2 = 4.86$ |
| $K_3 = 3.37 \cdot 10^{-12}$ | $pK_3 = 11.47$ |

### DANK

Der Autor möchte auch an dieser Stelle der Firma Geigy, A.G., Basel, Schweiz für die gefällige Überlassung von höchst reinem, zu diesem Zwecke hergestellten Chromazurol S seinen besten Dank aussprechen.

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Eingegangen den 25. April 1961

# Separation of antimony(III) by ion-exchange

MARCZENKO[1] used Wolfatit-P cation exchange resin in its ammonium form for selective separation of copper from a bearing alloy containing tin and antimony; from a tartaric acid solution buffered with ammonia to pH 9, copper was quantitatively retained on the resin, but only 97–99% of the antimony and tin could be accounted for in the eluate.

Better results can be obtained with ZeoKarb-225 for the quantitative separation of antimony from other metals. We have previously reported[2] that with excess of tartaric acid (16 to 20 times the weight of antimony present), antimony(V) forms a stable anionic complex that completely escapes adsorption on ZeoKarb-225 in its hydrogen form, while copper(II), iron(III), cobalt(II) or cadmium(II) is quantitatively retained.

We have since observed that with a cation exchanger, separation of antimony(III) from other cations is more difficult, particularly with tartar emetic as the source of antimony. And with ZeoKarb-225 in the hydrogen form, larger quantities of tartrate (30 times the weight of antimony present) are necessary. Better results have been obtained with ZeoKarb-225 in the ammonium form, with which complete separation can be effected by use of much smaller amounts of tartrate (5–10 times the weight of antimony(III) from chloride solution; none with tartar emetic). This difference in behaviour is believed to be due to the difference in the stability of antimony(III)-tartrate complex and the difference in the adsorption affinity of the ZeoKarb-225 in the ammonium form, towards the complex. Under the optimum conditions, Cu(II), Ni(II), Co(II), Cd(II), Zn(II), Mn(II), Fe(III) or Cr(III) is selectively adsorbed on the resin from the respective binary mixture with antimony(III). The presence of all the antimony(III) as the anionic complex, was confirmed by quantitative adsorption on an anion exchanger (DeAcidite FF) from the eluate.

Separation of antimony(III) from synthetic mixtures with any of the above cations over a wide range of metal concentration (0.05 to 0.25 g of metal for 0.10 g of Sb), showed the method to be accurate to ± 1.0%.

## METHOD

### Reagents

*Tartar emetic solution*: A 3.0%(w/v) aqueous solution of the hydrated compound, standardized iodimetrically.

*Antimony trichloride solution*: 2–3 g of anhydrous $SbCl_3$ in 5% Rochelle salt solution or in 10% tartaric acid solution, standardized iodimetrically.

Other metal solutions were prepared from pure salts and standardized individually by conventional methods.

### Procedure

To a solution containing 0.05–0.10 g of antimony(III) and any of the above cations, add 0.25–0.50 g of Rochelle salt or 0.5–1.0 g of tartaric acid. Pass the solution at a slow rate (20–30 drops/min) through a column of ZeoKarb-225 (10–15 g in the ammonium form). Collect the percolate, wash the resin several times with distilled water and add the washings to the percolate. Analyse the combined solution for antimony(III) by the iodimetric method.

Elute the metal ion from the resin by passing aqueous hydrochloric acid (2–6 *N*) and analyse the eluate for the metal by a conventional method.

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[1] Z. MARCZENKO, *Chem. anal. (Warsaw)*, 2 (1957) 255.
[2] S. S. M. A. KHORASANI AND M. H. KHUNDKAR, *Anal. Chim. Acta*, 21 (1959) 406.

Received March 23th, 1961

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# Determination of traces of cyanide

Trace quantities of cyanides can be determined colorimetrically by conversion to a cyanogen halide followed by reaction with pyridine and a condensing agent such as benzidine[1], pyrazolone[2] or barbituric acid[3]. The colours developed in some of these reactions, however, tend to fade rapidly[4]. Further, in the latter two methods, the intermediate compound is cyanogen chloride (b.p. 13.8°), the use of which is not wholly satisfactory at high ambient temperatures owing to possible losses. We have found that by suitably adjusting the concentration of barbituric acid and replacing cyanogen chloride with cyanogen bromide it is possible to increase the stability of the colour complex considerably. The procedure described below has been worked out to suit the high ambient temperatures prevailing in the tropics.

## PROCEDURE

### *Mixed reagent*

Place 55 ml of redistilled A.R. pyridine in a 100-ml flask. Add 20 ml of 1 : 3 hydrochloric acid slowly with cooling followed by 30 ml of 0.8% barbituric acid solution. Dilute to the mark.

To 25 ml of a neutral or slightly acidic solution of cyanide (concentration range 0.01 to 1.5 $\mu$g/ml) in a stoppered vessel, add 1 ml of bromine water and mix. After 2 min add 0.5 ml of 2% arsenious acid and agitate to remove excess bromine. Add 10 ml of the mixed reagent and keep for 40 min at about 40°. Measure the optical density in a H 760 Spekker absorptiometer with Ilford spectrum filter No. 606. If the mixed reagent is freshly prepared, water alone may be used as blank. Use 4-cm, 1-cm and 0.5-cm cells in the ranges 0.01–0.2, 0.2–0.8 and 0.8–1.5 $\mu$g/ml respectively.

According to this procedure the decrease in optical density over a period of 200 min at 25° is about 1% of the original value whereas the benzidine and pyrazolone colours fade to the extent of 14% as determined by LUDZACK *et al*[4]. The higher sensitivity and superior stability of the colour developed by the present method as compared with that of ALDRIDGE[1] are clearly brought out in Fig. 1. The colour is also much more stable than that formed in the cyanogen chloride-barbituric acid method[3], where the determination should be completed in 15 min.

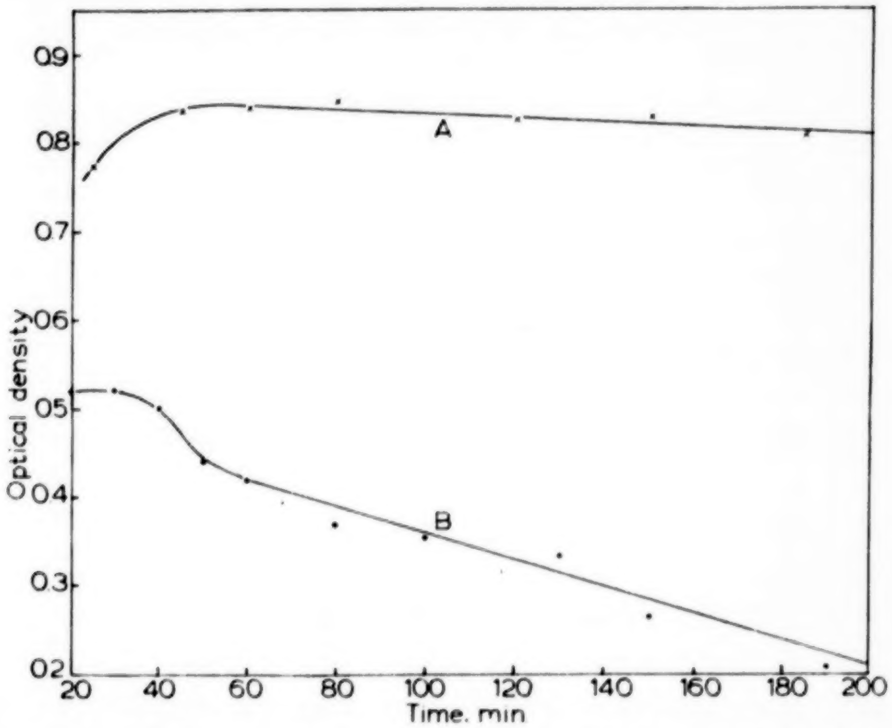

Fig. 1. Comparison of stability of colour. Cyanide concentration 0.6 μg/ml; temperarure 38°. Curve A: Present method using 606 filter. Curve B: Benzidine method using 604 filter.

TABLE I

ANALYSIS OF CYANIDE SOLUTIONS OF KNOWN CONCENTRATION

| *Concentration of cyanide taken μg/ml* | *Cyanide found μg/ml* |
|---|---|
| 0.010 | 0.011 |
| | 0.010 |
| | 0.011 |
| 0.050 | 0.047 |
| | 0.052 |
| | 0.050 |
| 0.150 | 0.156 |
| | 0.148 |
| 0.300 | 0.292 |
| | 0.314 |
| 0.543 | 0.536 |
| | 0.540 |
| | 0.532 |
| | 0.553 |
| | 0.543 |
| | 0.551 |
| 0.800 | 0.790 |
| | 0.820 |
| | 0.810 |
| 1.00 | 1.02 |
| | 1.01 |
| | 0.98 |

A few typical analyses obtained by the above method are given in Table I, from which it will be seen that the accuracy attainable is quite satisfactory. The coefficient of variation when analysing a solution of 0.543 $\mu$g/ml was 1.7 which compares very favourably with the figures for the other methods[4].

## ACKNOWLEDGEMENT

We are grateful to the Tata Iron & Steel Company for permission to publish this paper.

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*Steel Company, Jamshedpur (India)*

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[1] W. N. Aldridge, *Analyst*, 70 (1945) 474.
[2] J. Epstein, *Anal. Chem.*, 19 (1947) 273.
[3] E. Asmus and H. Garschagen, *Z. anal. Chem.*, 138 (1953) 414.
[4] F. J. Ludzack, W. A. Moore and C. C. Ruckhoff, *Anal. Chem.*, 26 (1954) 1784.

Received February 20th, 1961

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# A sensitive, rapid determination of inorganic phosphate in presence of labile phosphate esters

In a previous paper[1] a determination of phosphate by a modified method based on that of Berenblum and Chain was described. The method is very sensitive and a large excess of sulphate does not interfere, while labile phosphate esters are not hydrolysed because of the short duration of the action of the acid ammonium molybdate solution (less than 30 sec). A disadvantage of the method is the elaborate procedure, as the phosphate has to be extracted first with butanol–benzene, after which the mixture is washed with water and finally reduced by shaking with stannous chloride. The separatory funnel must therefore be opened, and the stopper rinsed, three times. The present paper describes a more convenient procedure.

In order to avoid rinsing, the stopper of the separatory funnel is altered to a small funnel. The reduction by shaking with a stannous chloride solution is replaced by reduction with this reagent in a homogeneous alcoholic phase.

If a large number (*e.g.* 10) of separatory funnels are attached to a revolving bar, 10 samples can be shaken simultaneously, which renders the method suitable for routine determinations. The objection of Mori and Nakamura[2] to the method of Berenblum and Chain, *i.e.* its being complicated and time-consuming, is met by these three improvements. Therefore, the method of Berenblum and Chain remains preferable to that involving a single phase, because of the hydrolysis which occurs in the single phase, and because of the great susceptibility to interference by sulphate ions.

### *Apparatus*

In the neck of the separatory funnel (Fig. 1) a hole (I) is made; opposite this hole lies a small groove(IV), similar to those in dropping bottles. The small funnel has a similar groove (II) in its solid lower half, and a hole (III) leading to the interior of the separatory funnel. When the two holes are placed opposite the grooves, liquid can be poured into the separatory funnel (via arrow B), while the air can escape (via arrow A). When the small funnel is turned through 90° the separatory funnel is closed and can be shaken. Degassing by turning the lower cock is no longer necessary. The whole apparatus is made water-repellent by treatment with Desicote.

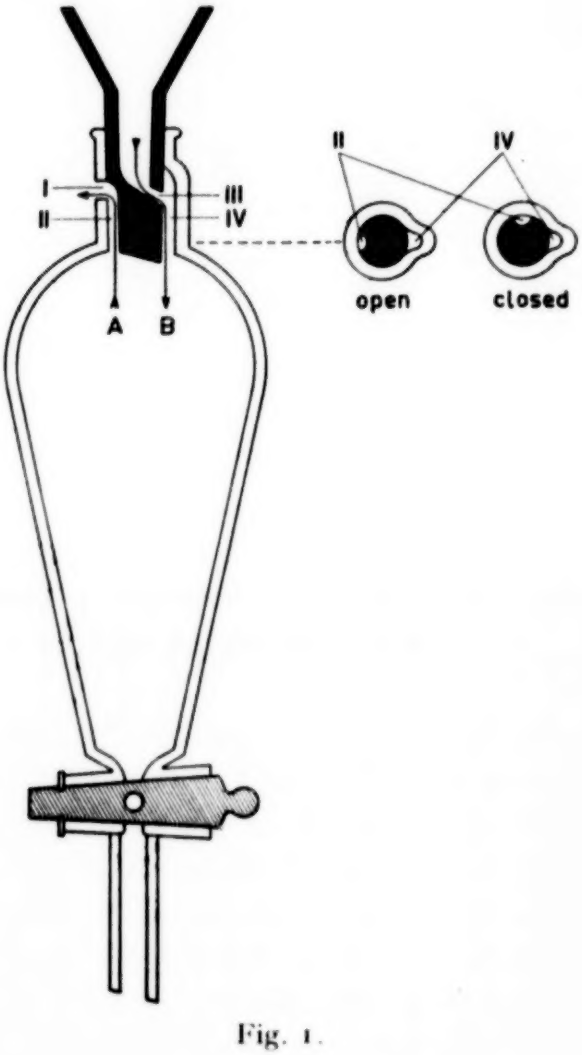

Fig. 1.

### *Reagents*

(*1*) Dissolve 5 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ *p.a.* in 100 ml of 2.5 *N* sulphuric acid. (*2*) Dissolve 5 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ *p.a.* in 100 ml of water. (*3*) Dissolve 2 g of hydrazine sulphate in 1 l of 0.6 *N* sulphuric acid, cool to about 10°, and add 1 g of stannous chloride. This solution becomes clear after about 12 h in a refrigerator and can be kept for about 4 weeks. (*4*) Isobutanol *p.a.* or distilled (fraction 107–108.5°).

### *Procedure*

To 25 or 35 ml of the sample add 5 ml of reagent (*1*), when the sample contains less than 12.5 mequiv. of sulphuric acid; add 5 ml of reagent (*2*) when it contains 12.5–24 mequiv. of sulphuric acid. Then introduce 15 ml of isobutanol into the separatory funnel. Close the funnel by turning the stopper through 90°, and shake. Then turn the stopper back and remove the lower layer. Shake the upper layer with 15 ml of 0.6 *N* sulphuric acid and subsequently rinse the upper layer with ethanol (96%) into a volumetric flask of $\alpha$ ml. While shaking the flask add $\alpha/100$ ml of the stannous solution (*3*) and dilute the contents to volume. Measure the extinction *e.g.* with a Zeiss Colorimeter ELKO III, filter 72. Depending on the amount of phosphate, $\alpha =$ 25, 50 or 100 ml.

When the concentration of phosphorus as phosphate is less than about 2 µg/25 ml, a larger sample must be used along with a proportionally larger amount of reagent (*1*) or (*2*). In this case 15 ml more of isobutanol than is required for saturation of the sample must be added. The other solutions are used in normal quantities. When, for example in limnology, determinations are carried out on samples of 500 ml, alcohols such as *n*-hexanol (or mixtures) are preferable, because they are less soluble in water. However, the time needed for the separation is then much longer. When more than 24 mequiv. of sulphuric acid is present, the surplus must be neutralised with sodium hydroxide. If more than 1 g of sodium sulphate is formed per 25 ml of sample, the sample must be extracted twice.

The method has been applied succesfully to sea-water. Even 5% of sodium chloride added to a phosphate stock solution in water does not interfere with the determination.

The amount of phosphate that can be determined in this way is equivalent to 1–200 µg of phosphorus. The calibration graph is straight in this range. The experimental error is about 1.5%.

The method is biochemically attractive because no interference arises from the hydrolysis of labile phosphate esters, nor from a large excess of sulphate or chloride. The latter quality and the great sensitivity (2 µg of phosphate-phosphorus in 500 ml) render the method suitable for limnology and oceanography.

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1 H. L. Golterman, *Acta Botan.*, 9 (1960) 1.
2 K. Mori and M. Nakamura, *Bull. Agric. Chem. Soc. Japan*, 23 (1959) 272.

Received June 3rd, 1961

## Book Reviews

H. Mattenheimer, *Mikromethoden für das klinisch-chemische und biochemische Laboratorium,* Walter de Gruyter & Co., Berlin, 1961, viii + 146 S., DM 16.—.

Der Autor gibt im vorliegenden Büchlein eine kurzgefasste Darstellung über modernes mikroanalytisches Arbeiten im klinisch-chemischen und biochemischen Bereich. Dabei wird zunächst auf allgemeine apparative und methodische Voraussetzungen mikroanalytischen Arbeitens eingegangen. In diesem Teil werden insbesondere viele für die Praxis wertvolle Hinweise gegeben. Im weiteren werden ausführliche mikroanalytische Arbeitsvorschriften zur Bestimmung klinisch-chemisch wichtiger Substanzen angegeben. Dabei werden in der Regel nur 50–100 $\mu$l Serum benötigt, was gegenüber den üblichen Methoden besonders dann wichtig ist, wenn nur wenig Blut zur Verfügung steht (z.B. in der Kinderklinik). Ein relativ breiter Raum ist der modernen enzymatischen Analyse von Metaboliten des Intermediärstoffwechsels und der Bestimmung der Aktivitäten von Serumenzymen gewidmet. Auch die hochempfindlichen fluorometrischen Bestimmungsmethoden der Pyridinnucleotide haben gebührende Berücksichtigung gefunden. Das Buch kann daher allen biochemisch arbeitenden Laboratorien als wertvolle Bereicherung ihrer Bibliothek empfohlen werden.

K. Krisch (Giessen/Lahn)

*Anal. Chim. Acta,* 25 (1961) 298

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*Treatise on Analytical Chemistry,* Édité par I. M. Kolthoff et P. J. Elving avec l'aide de E. B. Sandell, Part II, Vol. 1, *Chimie analytique des éléments,* 417 pp., 1961, Interscience Publishers, New York, prix US $16.00 (subscription price: US $14.00).

Nous avons déjà dit tout le bien que nous pensons de cet ouvrage et ce volume ne fait que confirmer cette opinion. Il débute par une innovation: un chapitre très complet sur toute la nomenclature inorganique présenté par W. C. Fernelius. Il est suivi par un exposé sur l'hydrogène (H. F. Beeghly) puis un vaste chapitre sur l'eau de J. Mitchell qui comprend aussi l'oxyde de deutérium et l'oxyde de tritium. On reste confondu en le parcourant, devant les possibilités infinies qu'offrent aux analystes, la physico-chimie et la physique. L'auteur donne plusieurs dizaines de méthodes quantitatives qui vont de la gravimétrie et la titrimétrie aux méthodes les plus récentes telles que la spectrométrie de masse, la résonance magnétique nucléaire et les méthodes radiochimiques basées sur l'emploi des neutrons, des rayons beta ou gamma.

Les gaz inertes sont l'oeuvre de G. A. Cook et les métaux alcalins présentés par S. Kallmann termine ce volume. A la fin de chaque chapitre, les auteurs donnent dans des paragraphes intitulés ***procédés de laboratoire recommandés*** un choix de méthodes reconnues avec un mode opératoire détaillé.

D. Monnier (Genève)

*Anal. Chim. Acta,* 25 (1961) 298

G. H. Osborn, *Synthetic Ion-Exchangers, Recent Developments in Theory and Application*, Chapman and Hall, London, 1961, 344 pp., price 50 s.

This book does not deal exclusively with analytical aspects of synthetic ion-exchangers, although 34 pages of clear concise information are contained under this heading. A further 120 pages, comprising what is, in effect, Part I of the book, contains chapters of almost equal interest to the analyst, including a detailed study of ion-exchange membranes and the use of ion-exchange resins in the control of trade effluents; in the section dealing with therapeutic applications, the reader is almost tempted to regard the human body as another form of ion-exchange column. The chapter devoted to large scale applications of these resins deals with such subjects as the production of hydrochloric acid from brine, glutamic acid from sugar beet, and the recovery of gold from cyanide liquors.

In this revised edition, some of the more theoretical sections contained in the first edition have been omitted, and the more practical aspects of the subject have been expanded.

As in the first edition the author has avoided presenting a maze of information with supporting references, which unfortunately so often happens when such a wide coverage is attempted, but has wisely chosen to continue to present such information in a separate, carefully prepared classified bibliography, comprising the second part of the book. This part in itself is a commendable feature of the publication; it contains some 500 more titles than were included in the first edition.

Anyone with a problem involving a chemical reaction, is advised to consult this book to ascertain the extent to which it might be resolved by the application of Synthetic Ion-Exchangers.

W. T. Elwell (Birmingham)

## Publications received

*Bibliography of Publications dealing with the Polarographic Method in 1959*, by Jaroslav Heyrovský. Nakladatelství Československé akademie věd, Praha, 1961, 96 pp. Price 6.30 Kčs.

## Announcements

### 1962 PITTSBURGH CONFERENCE

### PRELIMINARY ANNOUNCEMENT

The Thirteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Penn-Sheraton Hotel in Pittsburgh, Pennsylvania, U.S.A., March 5–9, 1962. Approximately 200 papers on all phases of analytical chemistry and spectroscopy will be presented. A symposium entitled *Raman Spectroscopy* will be sponsored jointly with the Coblentz Society, and a symposium entitled *Vacuum Spectroscopy* will be co-sponsored with the Society for Applied Spectroscopy. Symposia entitled *Gas Chromatography*, *Spectroscopic Studies of Polymers*, and *Chemical Analysis of Metals* will also be held.

Original papers on all phases of analytical chemistry and spectroscopy are invited. A brief abstract (150 words) of each paper will be printed in the program. Three copies of this abstract, with a letter listing the names of the authors, the laboratory in which the work was done, and the current addresses of the authors, should be addressed to: Dr. CHARLES F. GLICK, Program Chairman, The Thirteenth Pittsburgh Conference, Applied Research Laboratory, U.S. Steel Corporation, Monroeville, Penna., U.S.A.

Final date for receipt of abstracts is October 16, 1961. One copy of the complete paper must be submitted by January 1, 1962.

In addition to the program of technical papers, there will be an exhibition of the newest analytical instrumentation. More than 110 companies will display instruments, chemicals, and equipment.

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# SYMPOSIUM INTERNATIONAL DE CHIMIE ORGANIQUE

*Bruxelles*

*11–14 juin 1962*

À l'occasion du 75e anniversaire de sa fondation, la Société Chimique de Belgique organise à Bruxelles, du 11 au 14 juin 1962, un

*Symposium International de Chimie Organique*
*consacré à l'Étude des Produits Naturels,*
*à l'exclusion des Stéroïdes et des Polypeptides.*

Les travaux de ce Congrès qui se tiendra sous les auspices de l'Union Internationale de Chimie Pure et Appliquée (I.U.P.A.C.), seront répartis en 5 Sections, de la manière suivante:

(*1*) Détermination de la structure de produits naturels nouveaux; (*2*) Méthodes d'investigation structurale — Apports nouveaux; (*3*) Synthèses et réactions chimiques (à l'exclusion des réactions de dégradation); (*4*) Hypothèses biogénétiques; (*5*) Mode d'action des produits naturels intervenant dans les processus biologiques.

Il est en outre prévu 7 conférences plénières, soit 5 dont le sujet se rapportera successivement à chacune des Sections, une conférence d'ouverture et une de clôture du Congrès.

*Secrétariat du Symposium*: Mr. FLORENT MARTIN, D.Sc., 68, rue Berkendael, Bruxelles 6 (Belgique), Téléphone 43.01.17 (225–255).

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 25, No. 4, October 1961

## AN EXAMINATION OF SOME ASPECTS OF INCREASING SELECTIVITY IN CHELATOMETRY

*(Review)*

T. S. West, *Anal. Chim. Acta*, 25 (1961) 301–312

## PAPER SOLUBILIZATION CHROMATOGRAPHY

### I. PHENOLS

The $R_F$ values of a series of eleven phenols have been determined using paper-chromatographic techniques on filter paper loaded with ion-exchange resin. The data have been used to predict the separation of various mixtures of these phenols by development with aqueous solutions of acetic acid.

D. Locke and J. Sherma, *Anal. Chim. Acta*, 25 (1961) 312–316

## SEMI-MICRO CRYOSCOPIC MOLECULAR WEIGHT DETERMINATION WITH A THERMISTOR THERMOMETER

An apparatus for extending the steady state freezing point depression method to small volumes, of the order of 0.3 or 0.4 ml, has been developed. A thermistor is used as the temperature sensing element, in one arm of a Wheatstone bridge. The apparatus is simple and dependable. Accuracies in the order of 2% are easily attainable.

J. A. Knight, B. Wilkins Jr., D. K. Davis and F. Sicilio, *Anal. Chim. Acta*, 25 (1961) 317–321

## DIFFERENTIAL PRECIPITATION IONOGRAPHY FOR QUALITATIVE CATION ANALYSIS

A method — differential precipitation ionography — is described for the separation and detection of cations in mixtures in trace amounts. The ions are caused to migrate by application of current to a supporting membrane. The substrate is kept moist with an electrolyte so chosen that its electrolysis provides a pH gradient. The migrating ions form narrow bands of their oxides or hydroxides at the point of their precipitation pH in this field. After this separation the filter is developed with a suitable reagent and examined microscopically. Several metal ions can be detected in a single sample. Materials in amounts as low as $10^{-9}$ g may be detected.

B. J. Tufts, *Anal. Chim. Acta*, 25 (1961) 322–327

## ORGANIC COMPOSITION ANALYSIS BY COMBINATION OF GAS CHROMATOGRAPHY WITH INFRARED SPECTROPHOTOMETRY

A technique combining gas chromatography with infrared spectrophotometry for analysis of complex organic mixtures has been described and modes of application discussed. The components are trapped and run as gases. Proper use of the data makes possible qualitative and quantitative analysis.

W. L. Senn Jr. and H. V. Drushel, *Anal. Chim. Acta*, 25 (1961) 328–333

## THE ABSORPTIOMETRIC DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS

A critical investigation has been made of the vanadomolybdiphosphate method for the absorptiometric determination of phosphorus in irons and steels. The reaction conditions have been standardised to produce a simple, rapid and reliable control method. The effects of interfering elements have also been studied.

G. Lindley, *Anal. Chim. Acta*, 25 (1961) 334–342

## OXIMIDOBENZOTETRONIC ACID

### A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

Oximidobenzotetronic acid is proposed for the spectrophotometric estimation of iron. A freshly prepared alcoholic solution of the reagent produces a deep blue water-soluble complex with an aqueous solution of iron(II). The complex is stable and its optical density is constant at pH 2.5–10. Lambert-Beer's law is followed from 0.54–5.4 p.p.m. of iron at 625 m$\mu$; temperature has no effect between 10° and 50°. The reagent is highly selective for iron.

A. N. Bhat and B. D. Jain, *Anal. Chim. Acta*, 25 (1961) 343–347

## SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF METALS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

PAN(1-(2-pyridylazo)-2-naphthol) is proposed for the solvent extraction and spectrophotometric determination of manganese, iron, cadmium, mercury, gallium and yttrium. The reagent, which is highly specific for iron, has been applied to the determination of iron in clay and anorthosite. The separation of yttrium from lanthanum and the separation of manganese from nickel were successful.

S. Shibata, *Anal. Chim. Acta*, 25 (1961) 348–359

## STUDIES ON THE EXTRACTION OF ZIRCONIUM WITH ORGANOPHOSPHORUS COMPOUNDS

The extraction of zirconium from nitric acid media with alkyl phosphates, phosphonate, phosphinate and phosphine oxide was studied. The extraction ability is affected by alkyl substituents attached to the phosphoryl group as well as by the solvent structure, the order of efficiency being: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec*-butyl phosphate > diethyl butyl phosphate > normal alkyl phosphates. In the extraction with normal alkyl phosphates, two solvent molecules and four nitrate ions combine with one atom of zirconium. The equilibrium constant and the effect of temperature were studied in the extraction with tri-*n*-butyl phosphate. The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with the organophosphorus solvents were measured; it was confirmed that a covalent complex was formed.

H. Umezawa and R. Hara, *Anal. Chim. Acta*, 25 (1961) 360–365

## SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH STANNOUS IODIDE REAGENT

The tin(II) iodide reagent reacts with rhodium to form a stable colored complex with an absorption maximum at 460 m$\mu$. The system obeys Beer's law and exhibits a molar absorptivity of $3.9 \cdot 10^4$ at 460 m$\mu$. Rhodium concentrations between 0.4 and 3 p.p.m. can be determined with an average deviation of only 0.3%. The method compares favorably with the tin(II) chloride and bromide methods for rhodium and is considerably more sensitive. Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni and Fe interfere with the method. Consequently, just as is the case with the chloride and bromide reagent, Rh must be separated from most samples prior to an analysis.

E. W. Berg and H. L. Youmans, *Anal. Chim. Acta*, 25 (1961) 366–370

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## REFERENCE ELECTRODES FOR VOLTAMMETRY IN ACETONITRILE

The saturated calomel electrode is *the* reference electrode in aqueous polarographic studies. Such is not the case, however, with nonaqueous polarographic studies. In particular acetonitrile has been used as the solvent for many polarographic studies with just as many reference electrodes. An attempt has been made to correct this unfortunate situation. Appropriate measurements have been made to evaluate the potential of the various reference electrode systems used in acetonitrile with respect to the aqueous saturated calomel electrode.

R. C. Larson, R. T. Iwamoto and R. N. Adams, *Anal. Chim. Acta*, 25 (1961) 371–374

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## APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

### II. TIN-BASE ALLOYS

Electrodeposition methods are described for the determination of antimony, copper and lead in tin-base alloys and a method for the determination of tin by controlled-potential electrolysis is discussed.

B. Alfonsi, *Anal. Chim. Acta*, 25 (1961) 374–378

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## POLAROMETRIC DETERMINATION OF AROMATIC ALDEHYDES WITH 2,4-DINITROPHENYLHYDRAZINE

In the polarometric titration of aromatic aldehydes with a 2,4-dinitrophenylhydrazine solution, the sorption of the reagent on the hydrazone precipitate and the reduction of this precipitate at the mercury dropping electrode have been proved. These effects may be eliminated by the addition of thymol or ethanol to the sample solution, so that most aromatic aldehydes can be determined.

A. Berka, J. Doležal, J. Janata and J. Zýka, *Anal. Chim. Acta*, 25 (1961) 379–385

## RAPID DETERMINATION OF ALUMINIUM IN BERYLLIUM METAL BY CATHODE RAY POLAROGRAPHY

A rapid method is presented for the determination of aluminium in beryllium metal by cathode ray polarography using the dye Superchrome Garnet Y. A mercury cathode electrolysis is used to remove heavy metal impurities, but the need for a separation of aluminium from beryllium is avoided. A single determination requiring a 100-mg sample may be completed in little over an hour, with normal polarographic precision.

T. M. FLORENCE AND D. B. IZARD, *Anal. Chim. Acta*, 25 (1961) 386–389

## SIMPLE DISTILLATION METHOD FOR TITRIMETRIC DETERMINATION OF CARBON DIOXIDE

*(in German)*

Carbon dioxide can be distilled at atmospheric pressure if the cooling is properly controlled. A suitable procedure is described. Interference from atmospheric carbon dioxide is prevented by the use of pentane as sealing liquid. Titrations with 0.01–0.1 *N* solutions allow determination of 0.22–22 mg of carbon dioxide with an accuracy of ±2–0.2%.

L. MAROS, E. SCHULEK, I. MOLNÁR-PERL AND M. PINTÉR-SZAKÁCS, *Anal. Chim. Acta*, 25 (1961) 390–399

## A SPECIFIC AND SENSITIVE SPOT TEST FOR CADMIUM UTILIZING GLYOXAL-BIS(2-HYDROXYANIL)

A test for cadmium based on the use of glyoxal-bis(2-hydroxyanil) is proposed. The reaction is carried out on beads of an anion exchange resin on which the cadmium has been concentrated as the tetraiodo complex. Separations inherent in the procedure make the test specific. The limit of identification is 0.05 μg.

PH. W. WEST AND J. DIFFEE, *Anal. Chim. Acta*, 25 (1961) 399–402

## DETERMINATION OF TRACES OF WATER IN GASES BY MEANS OF A MODIFIED KEIDEL ELECTROLYTIC HYGROMETER

*(Short Communication)*

E. BARENDRECHT, *Anal. Chim. Acta*, 25 (1961) 402–404

## DETERMINATION OF MAGNESIUM AND ALUMINIUM IN ZINC-BASE DIE-CASTING ALLOYS

*(Addendum)*

L. BLOCH, *Anal. Chim. Acta*, 25 (1961) 404

**Review**

# AN EXAMINATION OF SOME ASPECTS OF INCREASING SELECTIVITY IN CHELATOMETRY*

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(Received March 18th, 1961)

The evolution of ethylenediaminetetraacetic acid and related compounds as analytical reagents by SCHWARZENBACH and his co-workers and the subsequent development by him and many other capable workers, notably PŘIBIL, FLASCHKA, REILLEY AND RINGBOM, has undoubtedly revolutionized the face of inorganic analysis. Rapid, and on the whole, trustworthy titrimetric procedures based on the use of EDTA are available for practically all metal ions except beryllium and some of the platinum metals and indirect methods for many of the non-metals. Yet EDTA is undoubtedly one of the most unselective organic reagents ever proposed for inorganic analysis and it is only by the ingenious use of a large number of auxiliary chemical reactions that such rapid progress has been made possible during the last decade in applying the procedures to the analysis of mixtures and commercial materials. Now the situation may be viewed as consolidated and the chief problem remaining is to simplify matters by increasing the selectivity of reaction wherever possible.

In the following paper some of the newer aspects of complexometry are discussed with particular reference to the problem of increasing selectivity. It should be noted, however, that advantages to be gained by the use of instrumental methods of detecting the end-point have not been taken into consideration nor has the use of polyamines as titrants.

There are three main avenues open to exploration in searching for increased selectivity. Briefly stated, these are as follows:

(*1*) The development of more selective reagents of the complexan type.
(*2*) The development of selective indicators.
(*3*) The development of selective masking agents.

Neither of the first two developments is of much practical use without the other, as will be instanced later on in the discussion, for a selective complexan cannot be of much use in conjunction with the conventional type of metallochromic indicator which is highly unselective. The converse is also true. Most of the progress so far made in obtaining selective complexometric titration without recourse to physical methods of separation has been made possible only as a result of the use of masking agents.

The three major avenues of approach to the problem having been delineated, each may now be investigated in turn.

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* Paper presented on 24th January at the 14th Annual Symposium on Analytical Chemistry, Louisiana State University, 1961.

### *A. Chelating agents*

If a complexan is defined as a derivative of iminodiacetic acid (Fig. 1), it will be seen at once that any hopes of obtaining high selectivity of reaction from such a reagent are rather remote, for this group is a complex former *par excellence* by virtue of its multidentate nature, its disposition of lone-pair electrons, steric make-up, etc. Consequently reagents based on it are likely to have a high affinity for the majority of cations, even for the strongly electropositive cations of the alkalies and alkaline earths. Therefore, the best approach appears to be to cut down the reactivity of the group towards certain cations by introducing steric factors which will hinder the reaction of these metals with the complexan centre or, alternatively, to introduce other complex-forming centres in a position such that the metal atoms bound up in the chelate 'claw' of the complexan group can be coordinately bound to the new centre preferably in a five- or six-membered ring structure. This pattern can be traced in some of the following reagents.

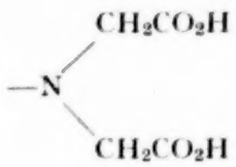
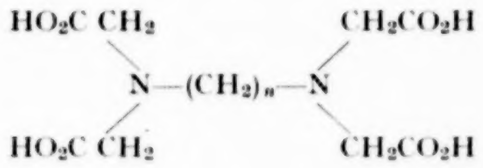


Fig. 1.

First of all, a steric factor has been applied neatly by SCHWARZENBACH and his co-workers[1] who produced homologues of EDTA with the number of carbon atoms between the two complexan centres increasing from 2–8. In EDTA ($n = 2$), the nitrogen atoms are situated so that they form a five-membered ring with the cation across the ethylenediamine bridge, but not unnaturally as the nitrogen atoms are moved further apart the effectiveness of the reagents falls off sharply from $n = 2$ through $n = 4$. As will be seen from Table I from $n = 4$ to $n = 8$ little change results for calcium and cadmium. However, with mercury(II) a different behaviour exists. The stability of the chelates first of all decreases slightly, but thereafter increases till at

TABLE I

HOMOLOGUES OF EDTA



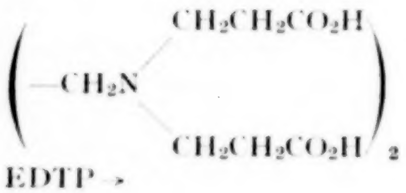
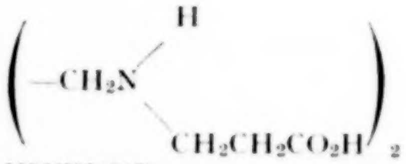
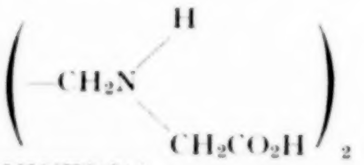
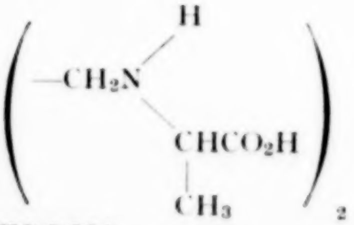
| *n* | *Log K* | | |
|---|---|---|---|
| | *Ca⁺²* | *Cd⁺²* | *Hg⁺²* |
| 2 | 10.59 | 16.62 | 21.8 |
| 3 | 7.12 | 13.45 | 19.7 |
| 4 | 5.05 | 11.87 | 20.8 |
| 5 | 4.60 | — | — |
| 6 | 4.40 | 11.70 | 21.38 |
| 8 | 4.51 | 11.99 | 21.83 |

$n = 8$ the reagent is, if anything, more efficient than EDTA. It is also noticeable that a slight increase occurs from $n = 6$ to $n = 8$ for the other metals. This may be due to the degree of flexibility which exists in an 8-membered carbon chain. It is tempting to try and advance a reason for the remarkable specificity of this reagent towards mercury(II). The construction of molecular models reveals no apparent structural difficulty for other metals to form chelates with the reagent equally as well as mercury (II). This rather casts doubt on the view that the selectivity may be due to the ease of deformation of the mercury(II) ion. However that may be, the information currently available points to this reagent, octamethylene diamine-N,N,N′,N′-tetraacetic acid (ODTA), as being very selective towards mercury(II).

Another interesting series of reagents which illustrates some useful steric and structural effects is shown in Table II (EDTA is included for ease of comparison). In ethylenediamine-N,N,N′,N′-tetrapropionic acid (EDTP) the size of the primary chelate ring has been increased by one methylene unit, though the five-membered ring across the ethylenediamine bridge remains. It will be seen that in comparison to EDTA the efficiency of chelation towards magnesium, cadmium and nickel falls off very markedly[2], but a high degree of reactivity is maintained towards copper(II). If now the effect of removing one of the acetic acid groups from each nitrogen atom in

TABLE II

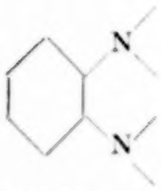
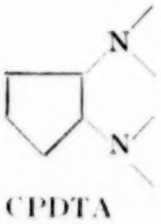
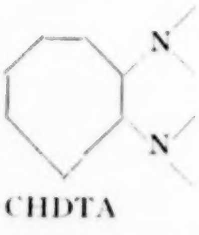
SIZE OF PRIMARY RING/STERIC HINDRANCE IN RING

| *Complexan* | *Log K* | | | |
|---|---|---|---|---|
| | *Mg* | *Cd* | *Ni* | *Cu* |
| EDTA → | 8.69 | 16.46 | 18.2 | 18.8 |
|  $(\text{—CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2)_2$ <br> EDTP → | 1.8 | 6.0 | 9.7 | 15.4 |
|  $(\text{—CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$ <br> NN′EDDP → | 1.6 | 5.6 | 9.3 | 15.1 |
|  $(\text{—CH}_2\text{N}(\text{H})\text{CH}_2\text{CO}_2\text{H})_2$ <br> NN′EDDA → | 3.9 | 8.8 | 13.5 | 16.2 |
|  $(\text{—CH}_2\text{N}(\text{H})\text{CH}(\text{CH}_3)\text{CO}_2\text{H})_2$ <br> EDDMA → | 2.8 | 8.1 | 12.2 | 16.2 |

EDTA is studied and also a similar procedure for EDTP, then the reagents thus obtained, ethylenediamine-N,N′-diacetic acid (EDDA)[3] and ethylenediamine-N,N′-dipropionic acid (EDDP)[2], still show a high reactivity towards copper(II) and reduced affinity for the other metal ions. The removal of the propionic acid group from each nitrogen atom in EDTP does not have a marked effect on the stability constants, thus indicating that the second propionic acid group probably plays little part in chelation by EDTP. The removal of an acetic acid group from each nitrogen atom in EDTA, however, does have a very pronounced effect on the stability constants of the magnesium and cadmium and, to a lesser extent, the nickel chelate. This tends to show that the oxygen atom of the carboxyl group plays a vital role in these EDTA chelates. Once more, however, it is apparent that this acetic acid group is unimportant in the chelation of copper(II). It may be concluded from all these results that the ring across the ethylenediamine bridge is a very decisive factor in the chelation of copper (II) and indeed this can readily be explained on the basis of the normal square coplanar habit of the copper(II) ion, for it would not be thus sterically possible for the copper(II) ion to unite with more than one acetyl group on each nitrogen atom as well as with the nitrogen atom itself. Furthermore, the decrease from EDTA to EDTP and from EDDA to EDDP suggests that the strength of the primary ring is of less importance than that of the N—CH$_2$—CH$_2$—N ring. Additional evidence for the latter idea may be drawn from the well-known copper reagents, most of which also contain a similar chain. The steric effect of the iso-propyl group in the reagent EDDMA has

TABLE III

COMPLEXANS WITH RESTRICTED ROTATION ABOUT N—CH$_2$—CH$_2$—N BOND

| *Complexan* | *Log K* | | | |
|---|---|---|---|---|
| | *Ca*$^{+2}$ | *Ba*$^{+2}$ | *Mg*$^{+2}$ | *Cu*$^{+2}$ |
| EDTA | 10.59 | 7.76 | 8.69 | 18.8 |
| <br>CDTA | 12.50 | 7.99 | 10.32 | 21.30 |
| <br>CPDTA | 11.2 | — | — | 19 |
| <br>CHDTA | 12 | — | — | 23 |

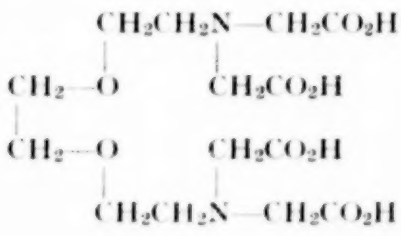
been studied by IRVING, SHELTON AND EVANS[4]. Again, there is high stability towards copper(II) and low affinity for magnesium, cadmium and to a lesser extent nickel. The steric hindrance of the —$CH_3$ group (comparison with EDDA) is negligible. All these reagents show a high degree of selectivity towards copper(II).

One of the most interesting of the complexans is *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid, first reported by SCHWARZENBACH and co-workers[5]. This reagent, CDTA, differs from EDTA in the attachment of a bulky group, but principally in the restriction of rotation about the ethylene bond. It was until recently, perhaps the most powerful complexan known. Now the cyclohexane ring can exist in boat and chair forms whereas the cyclopentane ring is planar and on the grounds of the entropy significance of this factor in subsequent chelation, MARTELL AND CALVIN[6] predict that CPDTA (1,2-diaminocyclopentane-N,N,N′,N′-tetraacetic acid) should be a yet more powerful reagent. Synthesis[7] and examination[8] of the reagent showed that perhaps this factor is less decisive than was originally thought (*cf.* Table III). The trio of reagents was completed by synthesis of the derivative 1,2-diaminocycloheptane-N,N,N′,N′-tetraacetic acid[7] (CHDTA), *i.e.* the higher homologue of CDTA. This proved to be stronger than CDTA for copper(II)[8] and to have virtually the same affinity for calcium[9]. There is little trend towards selectivity in these reagents, though it is possible that a certain degree of selectivity might be obtained on a kinetic basis, for these reagents are slow to react with some metal ions. However, their synthesis is difficult and costly, and it is not envisaged that they will have much practical importance. It is relevant to subsequent work described in this paper to note in passing that the stability constant gap between the calcium and barium chelates is greater with CDTA ($\Delta\,{}^{10}\log K = 4.51$) than with EDTA ($\Delta\,{}^{10}\log K = 2.83$). Thus a small measure of selectivity towards calcium relative to barium has been achieved in this particular reagent.

Yet another development is the incorporation of other chelating centres in the ethylenediamine chain. Thus (*cf.* Table IV) we have reagents such as the dioxygen

TABLE IV

COMPLEXANS WITH ADDITIONAL CENTRES



| *Complexan* | *Log K* | | | |
|---|---|---|---|---|
| | *Mg* | *Ca* | *Cd* | *$Hg^{+2}$* |
| EDTA | 8.69 | 10.59 | 16.46 | 21.8 |
| EGTA (O) | 5.2 | 11.0 | 16.73 | 23.2 |
| EGTA (S) | — | 4.87 | 13.57 | 23.93 |
| EGTA (N—$CH_3$) | 4.31 | 9.42 | 17.77 | 27.68 |

ether EGTA (O) (1 : 2-bis [2-di(carboxymethyl)aminoethoxy-]ethane)[1,10], its sulphur analogue — EGTA (S)[1], and the nearest approach to a nitrogen ether derivative where the oxygen atoms are replaced by N—$CH_3$ groups, EGTA (N—$CH_3$)[1]. EGTA (O) shows the influence of the oxygen atoms increasing the affinity towards calcium, cadmium and mercury(II) with a depressing effect towards magnesium. The thio ether EDTA (S) shows a depressing action towards all save mercury(II) whilst the =N—$CH_3$ group notably enhances cadmium and mercury(II). Again, from this series there are trends of selectivity towards mercury(II), cadmium (slight), and calcium, particularly in relation to magnesium. The difference in stability constants between the EGTA (O) chelates of calcium and magnesium is 5.8 $^{10}\log K$ units, whereas for EDTA it is only 1.9 units.

There are many other interesting trends towards selectivity to be observed, but obviously these cannot all be considered, though the high affinity towards iron(III) and copper(II) of ethylenediamine-N,N'-di(*o*-hydroxyphenylacetic acid)[11] and towards iron(III) of N,N'-bis(hydroxyethyl)ethylenediamine-N,N'-diacetic acid[12] in alkaline solution deserves special mention.

It should be pointed out, however, that a study of chelation constants can only serve as a useful guide and by no means gives a definitive answer as to what may happen in a solvent medium where other equilibria are involved. An interesting example of this occurs when solutions of the EDTA and NTA (nitrilotriacetic acid) chelates of iron(III) are treated with ammonia and a moderate excess of sodium sulphide. One would expect only to observe a difference in the degree of reaction, whereas, in practice a cherry-red complex is formed with the iron(III)–EDTA chelate and a very intense green complex with iron(III)–NTA. The former colour-body is not particularly stable whereas the latter, once formed, maintains an unchanged transmission for several hours. It may be used for the colorimetric determination of traces of iron, for the colorimetric determination of sulphide ion or as a spot test for either[13]. The results of this examination will be published at a later date.

### *B. Metallochromic indicators*

As mentioned previously, the benefit of selectivity of reagent cannot be reaped in a visual titration unless a selective indicator action is also available. Trends and developments of importance in this direction will now be discussed briefly.

In 1952–54 YOE AND RUSH[14,15] introduced zincon as a highly selective colorimetric reagent for copper(II) and zinc. Subsequently, KINNUNEN AND MERIKANTO[16] showed that at pH 10 only zinc could be titrated with EDTA and this reagent as indicator. The blue to yellow end-point is an attractive one, but unfortunately this does not provide a selective titration system for zinc, because even metals such as magnesium and strontium titrate partly with the zinc if they are present, whilst others such as calcium, cadmium and lead titrate completely. Obviously, however, if a selective complexan were available, advantage could be taken of the high selectivity of zincon as an indicator. The literature reveals some possibilities in this respect.

Fast Sulphon Black F (Fig. 2) was proposed by BELCHER, CLOSE AND WEST[17] as a highly selective indicator for the EDTA titration of copper. This bis-hydroxy bis-azo dyestuff is selected on the basis of the positioning of the hydroxyl groups with respect to the azo bond. The unusual *ortho-peri* position results in a larger chelate ring, a different stereochemistry across the azo bond and, of course, a different basicity of the phenolic oxygen. The disposition is such that only nickel and copper(II) react to form coloured chelates in alkaline solution and that only in the presence of ammonia. The indicator action with nickel against EDTA is too sluggish to be of any value, but the action with copper(II) is satisfactory; there again, metals such as calcium, cadmium, cobalt, titrate as copper(II) with EDTA even though they do not react with the indicator. Once more, however, a selective complexan would be of benefit and some of these have already been discussed.

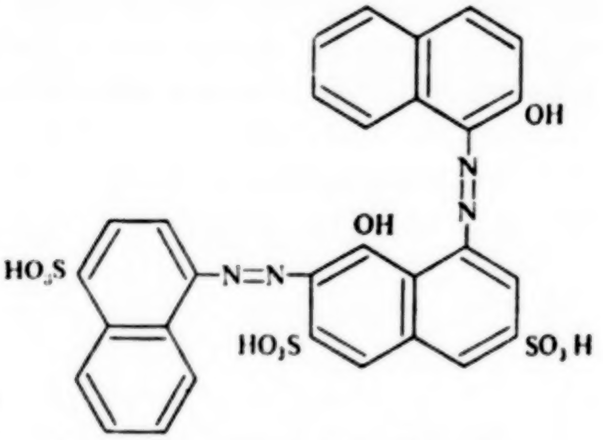


Fig. 2. Fast Sulphon Black F.

Glycine thymol blue, proposed by KÖRBL AND PŘIBIL[18] is not as selective as the two previously mentioned reagents, but it achieves a fair degree of selectivity by utilising a glycine group rather than an aminomethyldicarboxymethyl group substituted in a position vicinal to the protolysis centres of a conventional acid–base indicator. By this device, a good indicator action is obtained towards copper(II) in weakly acid solution. It does, however, also react with cobalt, cadmium, lead, zinc an mercury(II).

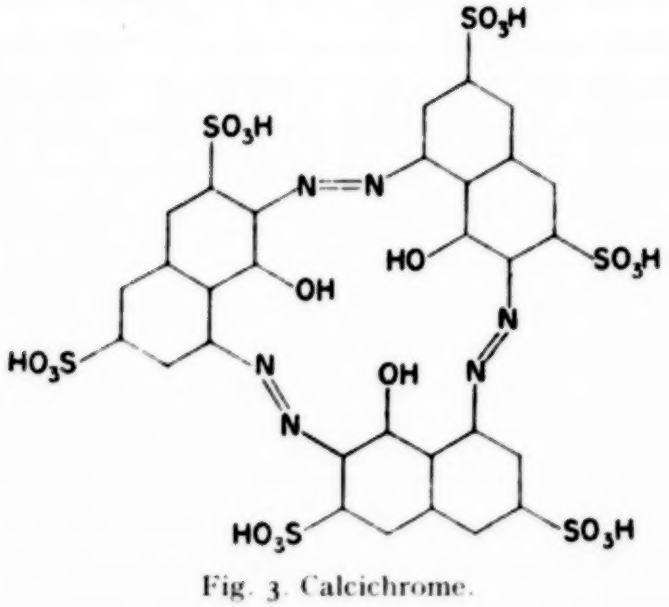


Fig. 3. Calcichrome.

Metallofluorescent indicators have recently received considerable attention. So far they do not show any trend towards specificity of reaction so mention is made only of two here. These are calcein blue, devised by WILKINS[19], which is a very good indicator for copper(II) ions, but may be used for others such as calcium, etc., and *o*-dianisidine-N,N,N',N'-tetraacetic acid synthesised by BELCHER, REES AND STEPHEN[20] which has a similar range of utility. These reagents should prove very valuable for the analysis of darkly coloured solutions or the titration of ions which form highly coloured complexan chelates.

Calcichrome (Fig. 3) synthesised and applied by CLOSE AND WEST[21], embodies most of the attractive features of *o*-hydroxyazo dyestuffs, *e.g.* high chromogenic capacity and low stability of metal complex, and dispenses with their chief drawback, lack of selectivity. This has been achieved by arranging the reactive groups in the centre of the molecule so as to form a chelate cage into which only certain ions can fit. This indicator is specific for calcium at pH 12 in a sodium hydroxide medium. Though chemical affinity may well have a role to play in the specificity of this reaction, the governing factors are undoubtedly (*a*) the ionic size of calcium ($r$ = 0.99 Å) as opposed to strontium (1.12 Å) and barium (1.34 Å), and (*b*) the fact that at this pH, metal ions other than these exist in an anionic form, or are precipitated out of solution. Calcium forms a red chelate with the molecule whereas barium and strontium do not appear to react. Thus the reagent may be used in a sensitive specific spot-test for calcium or it may be used as a complexometric indicator.

The development of this reagent suggested the possibility of its use as a metallochromic indicator for the titration of calcium in the presence of the other alkaline earths. For EDTA the stabilities of the calcium and barium chelates are ${}^{10}\log K = 10.59$ and 7.76 respectively (*i.e.* $\Delta\,{}^{10}\log K = 2.83$) so that the barium titrates with the calcium. However, for 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA) the corresponding values for $\log K$ are 12.50 and 7.99 ($\Delta\,{}^{10}\log \mathrm{K} = 4.51$). This separation, though not as much as could be desired, allows the titration by CDTA of calcium in the presence of much barium without the necessity of carrying out a separation. The stability constant of the strontium chelate of CDTA probably lies around $\log K \approx 10$ so that the strontium interferes in the titration of calcium, but a less precise titration may still be effected if some ammonium sulphate is added to precipitate the bulk of the strontium. This method[21] illustrates the effectiveness of using a selective complexan in conjunction with a specific indicator.

Another interesting example arises from the work of SADEK, SCHMID AND REILLEY[22]. The EDTA titration of calcium in the presence of magnesium must be carried out at pH ≈ 12 when magnesium hydroxide is insoluble, because the separation factor between the two EDTA chelates is only 1.9 log $K$ units. However, for EGTA (Table IV) the separation factor is 5.8 units and this presents a clear-cut possibility for the selective titration of calcium in the presence of soluble magnesium. No direct indicator is available, but REILLEY and his co-workers made ingenious use of a zinc-sensitised zincon indicator system for this purpose. Calcium reacts as follows when treated at pH 9.5 with zincon and a small amount of Zn-EGTA chelate.

$$\mathrm{Zn{-}EGTA^{-2}} + \mathrm{Ca^{+2}} \rightleftharpoons \mathrm{Zn^{+2}} + \mathrm{Ca{-}EGTA^{-2}}$$

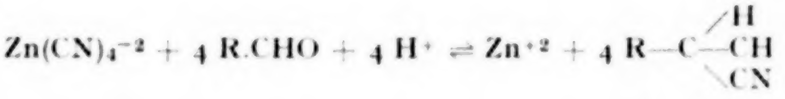
$$\underset{\text{(Yellow zincon)}}{\mathrm{HIn^{-3}}} + \mathrm{Zn^{+2}} \rightleftharpoons \underset{\text{(Blue Zn–zincon)}}{\mathrm{ZnIn^{-2}}} + \mathrm{H^{+}}$$

Magnesium does not produce a similar reaction. Thus the solution maintains a blue colour till the end-point, when the EGTA titrant removes the free calcium ions. The experimental conditions for the effective operation of this titration are rather restricted, but it is an interesting example of selectivity based on combined indicator and complexan action.

Another interesting development is based on kinetic effects. A recent example[19] of this illustrates the EDTA titration of nickel in the presence of chromium(III). Chromium(III) forms a much more stable EDTA chelate than does nickel, but it reacts slowly whereas nickel reacts quickly. Thus, it is possible to titrate the nickel before the chromium(III) reacts. Addition of an excess of EDTA and standing or warming allows the combined total of chromium(III) and nickel to be obtained.

### *C. Masking action*

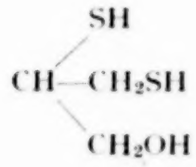
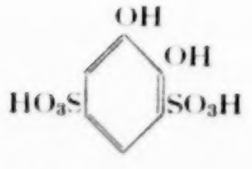
It is largely due to the use of masking agents that the technique of complexometric analysis has advanced to its present status, otherwise the methods would be useless for dealing with anything other than solutions containing only one species of metal ion. Consequently, this pathway towards selectivity is well-known and need not be surveyed in detail here. Some of the more common masking agents which screen selected groups of cations against reaction with EDTA are shown in Table V. The selective demasking of the cyanide complexes of cadmium and zinc is also well-known as a means of further increasing the selectivity, *i.e.*



$$Zn(CN)_4^{-2} + 4\ R.CHO + 4\ H^{+} \rightleftharpoons Zn^{+2} + 4\ R{-}C\begin{matrix}/H\\ {-}CH\\ \backslash CN\end{matrix}$$

TABLE V

SUMMARY OF MASKING ACTIONS

| *Masking agent* | *Cations masked* |
|---|---|
| KCN | $Ag^{+}$, $Cu^{+2}$, $Fe^{+2}$, $Hg^{+2}$, $Co^{+2}$, $Ni^{+2}$, $Zn^{+2}$, $Cd^{+2}$ |
| $N(CH_2CH_2OH)_3$ | $Fe^{+3}$, $Al^{+3}$, $Mn^{+3}$ |
|  | $Hg^{+2}$, $Cd^{+2}$, $Zn^{+2}$, $As^{+3}$, $Sb^{+3}$, $Sn^{+3}$, $Pb^{+2}$<br>$Bi^{+3}$<br>$Mn^{+2}$, $Fe^{+3}$, $Al^{+3}$ |
| $NH_4F$ | $Ca^{+2}$, $Mg^{+2}$, $Al^{+3}$, $Ti^{+4}$ (Nb and Ta) |
|  | $Al^{+3}$, $Ti^{+4}$, $Fe^{+3}$ |
| KI | $Hg^{+2}$ |
| $H^{+}$ | Various cations, *e.g.* $Ca^{+2}$, $Ba^{+2}$, $Sr^{+2}$ (pH $< 7$)<br>$Zn^{+2}$, $Cd^{+2}$, $Mn^{+2}$ (pH $< 2$) |
| Ascorbic acid | $Fe^{+3}$, $Cu^{+2}$ |

Amongst many newer masking agents not cited in Table V, the following deserve special mention: thiosemicarbazide[23] used to screen mercury(II) in presence of bismuth (pH 1–2), cadmium, zinc and lead; hydrogen peroxide[24] used for titanium(IV) in strongly alkaline solution; sulphosalicylic acid[25] used for aluminium and uranium (VI); acetyl acetone[25] used for aluminium. *o*-Phenanthroline[26] is useful for copper(II), cadmium, zinc, cobalt, nickel and manganese at pH 5–6; it does not complex lead or the rare earths.

Another useful and instructive adjunct towards increased specificity arises out of the use of liquid amalgams by SCRIBNER AND REILLEY[27]. For example, practically the only way to resolve a mixture of copper(II) and nickel by EDTA is to apply a reducing agent such as ascorbic acid. The use of a lead amalgam results in the reaction

$$Cu^{+2} + Ni^{+2} \xrightarrow{(Hg-Pb)} Pb^{+2} + Ni^{+2}$$

by which copper(II) is replaced by an equimolar amount of lead. The mixture of nickel and lead is easy to resolve by normal procedures. Conversely, difficult-to-mask ions can be replaced by others which are readily masked. Thus a mixture of lead and manganese(II) is difficult to resolve, but treatment with a zinc amalgam results in replacement of the lead by zinc in equimolar amount.

$$Pb^{+2} + Mn^{+2} \xrightarrow{(Zn-Hg)} Zn^{+2} + Mn^{+2}$$

This mixture is now easily resolved. Yet again, advantage may be taken of the difference between redox and complexometric equivalent weights which exists with metals such as bismuth. For example, both lead and bismuth react in 1 : 1 proportion with EDTA. If the solution is reduced with zinc amalgam and then titrated with EDTA, a different titre results because each lead ion is replaced by one of zinc and each bismuth ion is replaced by 1.5 zinc ions. Hence solution of the two simultaneous equations allows a complete resolution of this otherwise difficult mixture.

$$T_1 = [Pb^{+2}] + [Bi^{+3}] \quad \text{direct titration with EDTA}$$
$$T_2 = [Pb^{+2}] + 1.5\,[Bi^{+3}] \quad \text{titration with EDTA following reduction}$$

Finally, it is not inappropriate here to draw attention to one of the most selective reactions devised in the study of complexometry even though this is not a direct complexometric procedure in the normal sense of the word.

In 1954, ANDEREGG, FLASCHKA, SALLMANN AND SCHWARZENBACH[28] conceived the neat idea of utilising the acid–base properties of a conventional acid–base indicator (*o*-cresolphthalein) for complexometric purposes by introducing a complexan group in a position vicinal to the protolysis centre of the molecule. This produced the reagent commonly known as 'phthalein complexone' or 'metalphthalein'. Others subsequently explored this region, notably KÖRBL AND PŘIBIL[29] with their reagent Xylenol Orange. A similar group of reagents is based on the hydroxyanthraquinone series. One of these, commonly known as Alizarin complexan[30] (Fig. 4) has properties similar to Xylenol Orange, but may be used in the basic region as well, and functions best at a slightly lower pH than Xylenol Orange in acid solution where, for example, it is a particularly effective indicator for copper(II).

The reagent forms a red 1 : 1 chelate with cerium(III) which is not broken down by EDTA and in the course of further examination it was found not to be broken down by fluoride but indeed to form a new blue-coloured complex with it.

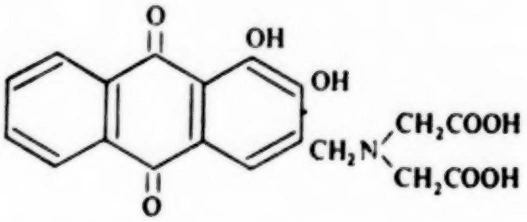


Fig. 4. Alizarin complexan (3-amino-methylalizarin-N : N-diacetic acid).

This complex has a composition corresponding to one part each of fluorine, cerium(III) and Alizarin complexan. The colour reaction is very sensitive and may readily be used for the spot-test detection of 0.2 $\mu$g of fluorine at a dilution limit of 1 : 1,800,000[31] or for the quantitative absorptiometric determination of $\mu$g[32] to mg[33] amounts (pH 5.2) of fluorine. This is probably the first reaction of the fluoride ion known in which a new coloured entity has been produced. All previous tests depend on bleaching or liberation of a free dyestuff from a metal-lake. However, the most surprising thing is the specificity of the reaction, for no other anion save fluoride is effective and the only metals to produce the reaction with fluoride and Alizarin complexan are the elements at the beginning of the lanthanon series, *viz.* La (At. No. 57), Ce (At. No. 58), Pr (At. No. 59) when the entry of the first 5d electron in La leads to subsequent filling of the 4f level throughout the lanthanon series. The mechanism of the reaction has been discussed elsewhere[34] and it has been shown that the blue complex produced by fluoride owes its colour to induced deprotonation of the organic part of the molecule following entry of the fluoride ion into one of the two remaining free ($H_2O$) coordinate positions of cerium(III) ion bound to the alizarin complexan.

None of the common anions interferes seriously with the procedure and though most metal cations do, their interference at the 1/1 level can be eliminated[33] by masking with cyanide, sulphide or iodide. Only in a few cases is it necessary to resort to solvent extraction with 8-hydroxyquinoline and chloroform. Preponderant amounts of metal ions would, no doubt, require physical separation in almost all cases.

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# PAPER SOLUBILIZATION CHROMATOGRAPHY

## I. PHENOLS

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(Received February 6th, 1961)

### INTRODUCTION

Solubilization chromatography, a technique whereby water-insoluble non-electrolytes are separated by elution with aqueous solutions of organic solvents through a column of ion-exchange resin, has been used to separate mixtures of alcohols and phenols[1]; ketones[2]; and ethers, carboxylic acids, and hydrocarbons[3]. This paper is the first in a series in which the methods of solubilization chromatography and conventional paper chromatography have been combined and applied to the separation of such compounds. It demonstrates the separation of various phenols on filter paper impregnated with ion-exchange resin by development with aqueous solutions of acetic acid. Future papers in the series will deal with separations of the other classes of compounds, not as derivatives, as well as studies of the effects of many of the variables involved in the process.

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## EXPERIMENTAL

Chromatograms were developed by the downward flow of solvent in a bench-top Chromatocab (Research Specialities Co., Model C-350). Amberlite SA-2 ion-exchange papers (batch No. 7802) were used in sheets 18 in. long by about 8 in. wide exactly as supplied in most cases (Rohm and Haas Co.). This paper contains about 45% by weight of Amberlite IR-120 strong-acid cation-exchange resin in the sodium form. For the few runs in which hydrogen-form paper was used, the sodium-form paper was soaked overnight in a 4% solution of reagent-grade hydrochloric acid, rinsed with distilled water, and dried before using.

All the phenols used in this study were of the best grade commercially available. All were used without further purification except catechol and *p*-hydroxybenzoic acid, which were recrystallized from ethanol, and the cresols, which were distilled. Developing solvents were prepared by dilution of reagent-grade glacial acetic acid and reagent-grade methanol.

Samples were transferred to the paper by means of a loop of platinum wire which delivered 5 $\mu$l of test solution (0.2 g/100 ml). The spots were dried after application by hanging the paper in a hood and using a hair drier. The $R_F$ values of Table I were determined by developing samples of each phenol with each of the different solvents. One chromatogram was sufficient to obtain the $R_F$ values of all eleven phenols at any given concentration of acetic acid by spotting the individual phenols across the top of the paper three-quarters of an inch apart; 3.5–4.5 h were required for the solvent front to travel to within one inch of the bottom of the paper sheet. Pre-equilibration of the chamber prior to development was not necessary since only one-phase solvents were used. Using the data of Table I, it was possible to calculate any possible separations. Several such separations of synthetic mixtures (10 $\mu$g of each component) were accomplished. Positive identification of the constituents was guaranteed by developing reference spots on the same piece of paper.

At the end of the solvent development, the chromatogram was removed from the tank and the solvent front marked. The solvent was dried off with the hair drier. To visualize the spots on the paper, it was sprayed with a reagent consisting of equal volumes of 5% ferric chloride and 1% potassium ferricyanide (by weight, in water). This solvent was found to be better than the one containing equal volumes of 1% solutions of each salt as suggested by BARTON *et al.*[4]. The paper was then steamed for 5 min after which time a blue color appeared to mark the location of the phenols. After a period of time, the entire background turns blue so that the positions of the spots should be immediately marked. The blue spots are the result of the reaction of ferricyanide with the divalent 1:1 complex formed between ferric ion and the phenol[5].

## RESULTS AND DISCUSSION

In the interpretation of results, use is made of the familiar equation

$$R_F = \frac{\text{distance travelled by leading edge of solute zone}}{\text{distance travelled by solvent front}} \qquad (1)$$

Table I lists the $R_F$ values as calculated by eqn. (1) for each of the phenols studied at different molarities of acetic acid. For most of the phenols, the spots measured one inch in length at all concentrations of acetic acid; resorcinol and *p*-hydroxybenzoic acid measured $1\frac{1}{4}$ in. and *p*-cresol and *m*-cresol measured $1\frac{1}{2}$ in. at all concentrations. Phloroglucinol and pyrogallol cometed over the entire length of the paper with all solvents and so could not be included in any of the synthetic mixtures later separated.

An inspection of the data of Table I indicates that the series of solvents studied tends to have a similar effect on any given phenol. That is to say, plots of $R_F$ *vs.* molarity of acetic acid for the various phenols would be almost parallel straight lines with about the same positive slope. A consequence of this is that the separability of a mixture of the phenols possible with any given solvent cannot be enhanced by changing solvents, as was found with solubilization chromatography in columns. If plots of $R_F$ *vs.* $M$ had been a group of crossing straight lines with widely varying slopes, changing solvents would probably have been of great aid in achieving separations.

TABLE I

| *Compound* | *Values of $R_F$ for [HAc]:* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *0.0 M* | *1.0 M* | *2.0 M* | *3.0 M* | *4.0 M* | *5.0 M* | *6.0 M* | *7.0 M* | *8.0 M* |
| catechol | 0.36 | 0.41 | 0.47 | 0.52 | 0.57 | 0.60 | 0.63 | 0.71 | 0.72 |
| *o*-cresol | 0.44 | 0.47 | 0.50 | 0.55 | 0.62 | 0.70 | 0.75 | 0.78 | 0.84 |
| *p*-cresol | 0.28 | 0.36 | 0.42 | 0.47 | 0.55 | 0.63 | 0.69 | 0.76 | 0.83 |
| *m*-cresol | 0.39 | 0.41 | 0.44 | 0.58 | 0.64 | 0.68 | 0.72 | 0.78 | 0.85 |
| *p*-hydroxybenzoic acid | 0.14 | 0.19 | 0.26 | 0.32 | 0.40 | 0.48 | 0.55 | 0.64 | 0.69 |
| *o*-hydroxybenzoic acid | 0.04 | 0.07 | 0.10 | 0.18 | 0.25 | 0.33 | 0.46 | 0.56 | 0.62 |
| phloroglucinol | 0.30 | 0.35 | 0.44 | 0.47 | 0.53 | 0.59 | 0.63 | 0.64 | 0.67 |
| pyrogallol | 0.34 | 0.46 | 0.51 | 0.53 | 0.57 | 0.60 | 0.63 | 0.65 | 0.68 |
| resorcinol | 0.35 | 0.43 | 0.48 | 0.52 | 0.59 | 0.64 | 0.69 | 0.72 | 0.77 |
| *m*-nitrophenol | 0.15 | 0.20 | 0.28 | 0.33 | 0.42 | 0.51 | 0.62 | 0.65 | 0.68 |
| phenol | 0.40 | 0.47 | 0.51 | 0.56 | 0.63 | 0.68 | 0.75 | 0.79 | 0.83 |

The use of the data of Table I and one simple equation allows the determination of the separations possible at any given concentration of acetic acid. The equation

$$DR_{F_1} = DR_{F_2} + l + \Delta S \qquad (2)$$

can be used to calculate the $R_F$ value which a solute must have to be separable from another solute with a value $R_{F_1}$. In this equation, $D$ is the distance between the point at which the solutes are spotted and the point of farthest advancement of the solvent front; $l$ is the length of the spot formed by the solute with the larger $R_F$ value when the solvent has moved $D$ cm. $\Delta S$ is the distance between the back of the spot that moves the farthest and the front of the one which moves less far. With the apparatus used in this study, the effective length of the paper sheets used was only 15 of the overall 22-in. length; therefore, $D$ was taken as 15 in. $\frac{1}{4}$ in. was taken as the required value of $\Delta S$ for the separation of two spots to be considered complete.

It can be calculated in this way that many 4-component separations are possible at different concentrations of acetic acid. To check the usefulness of eqn. (2), the following 4-component separations were successfully carried out (10 $\mu$g of each phenol in a total volume of 5 $\mu$l in each case):

(*1*) Phenol, *p*-cresol, *o*-hydroxybenzoic acid, and *m*-nitrophenol completely separated by development with water.

(*2*) Phenol, *p*-cresol, *o*-hydroxybenzoic acid, and *p*-hydroxybenzoic acid completely separated by development with 2.0 *M* acetic acid.

(*3*) Phenol, catechol, *m*-nitrophenol, and *o*-hydroxybenzoic acid completely separated by development with 5.0 *M* acetic acid.

(*4*) Phenol, *o*-hydroxybenzoic acid, resorcinol, and *m*-nitrophenol completely separated by development with 7.0 *M* acetic acid.

Many other 4-component mixtures could have been separated with equal success. By use of a different apparatus, it would be possible to perform separations not possible on the 15 in. of paper available in the system used here, and a number of 5- and 6-component separations could surely be successfully accomplished. A rearrangement of eqn. (2)

$$D = \frac{l + \Delta S}{(R_{F_1} - R_{F_2})} \tag{3}$$

is useful for calculating the length of paper needed to separate any two components whose $R_F$ values are known. In this equation, $D$ is the length of paper needed for a given separation, $R_{F_1}$ is the $R_F$ value of the solute moving the farthest, and $l$ and $\Delta S$ are as defined above. It should be remembered that upon development over distances greater than 15 in., the sizes of the spots may be somewhat greater than those described above.

It was attempted to achieve some 5- and 6-component separations on the 15 in. of paper afforded in the present apparatus by the technique of multiple development, in which the chromatogram is developed, dried, and then redeveloped with the same solvent. These attempts were unsuccessful because the effective length of the paper remaining after the first development is only the original 15 in. minus the distance the solutes have moved. The relatively high $R_F$ values of the compounds studied caused too much of the paper to be used in the first development for a useful amount to be left for subsequent developments.

A study was made to evaluate the results which would be obtained if the resin in the paper was changed from the sodium form to the hydrogen form prior to chromatography. The test chromatogram was developed with 8.0 *M* acetic acid so that the results could be compared with the development on sodium-form paper with 8.0 *M* acetic acid. It would be with this solvent of highest hydrogen-ion concentration that the maximum amount of ion exchange would occur between the sodium-form paper and hydrogen ion of the solvent. It was found for the nine phenols studied that the difference between the $R_F$ value on the hydrogen-form paper and that on the sodium-form paper for a given phenol was usually about 0.05, the value on the hydrogen-form paper being always the higher. Interpretation of these results will be made in a future paper after a more complete study of the effect of the ionic form of the paper is made. The present study proved that the convenient practice of using the ion-exchange papers as supplied in the sodium form in no way lessened the usefulness of the method as a separation tool even though a small amount of ion exchange between the paper and the solvent took place during each development.

The theory governing paper solubilization chromatography is even more complicated than that for solubilization chromatography on columns[3]. Even at low concentrations of acetic acid the phenols are virtually unionized and are separated by virtue of the differences in their partition between the moving solvent phase and the stationary phase. Interactions possible between the phenol molecules and the stationary phase include those with the resin particles (both ion-dipole and London dispersion forces), with the solvent inside the swollen resin particles, and with the paper itself. That the present process does differ from solubilization chromatography in columns is demonstrated by the fact that the order of elution from a strong-acid cation-exchange resin in the hydrogen form with aqueous acetic acid as eluent is catechol before phenol before *o*-cresol[3]. This means catechol has the least affinity for the resin, and *o*-cresol the most. On strong-acid, cation-exchange resin-loaded filter paper in the hydrogen form, *o*-cresol and phenol have the same $R_F$ values, and catechol a somewhat lower $R_F$. This means catechol has the greatest affinity for the ion-exchange paper. Furthermore, a preliminary study of the use of aqueous methanol rather than aqueous acetic acid as the developing solvent has shown that methanol has a displacing power no greater than water on the SA-2 paper used, whereas 1.0 *M* methanol proved to be a considerably better eluent than water in the conventional solubilization chromatography of the ketones[2]. It is hoped that more detailed studies of these and other variables in the future will clarify the mechanisms involved in both processes.

## ACKNOWLEDGEMENT

One of the authors (J.S.) would like to thank the Committee on Advanced Study and Research of Lafayette College for financial support of this project.

## SUMMARY

The $R_F$ values of a series of eleven phenols have been determined using paper-chromatographic techniques on filter paper loaded with ion-exchange resin. The data have been used to predict the separation of various mixtures of these phenols by development with aqueous solutions of acetic acid.

## RÉSUMÉ

Les auteurs ont effectué une série de déterminations de $R_F$ de onze phénols, par chromatographie sur papier, en utilisant un papier filtre, chargé de résine échangeur d'ions.

## ZUSAMMENFASSUNG

Es werden die $R_F$ Werte von 11 Phenolen bestimmt unter Verwendung eines Filterpapiers, das mit einem Ionenaustauscherharz beladen ist.

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# SEMI-MICRO CRYOSCOPIC MOLECULAR WEIGHT DETERMINATION WITH A THERMISTOR THERMOMETER*

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(Received January 8th, 1961)

## INTRODUCTION

The determination of molecular weights of small quantities of materials has wide applicability. A technique has been developed for the determination of the molecular weight of compounds with volumes as small as 0.3 ml of solution by the steady state freezing point method. The method can be refined to extend to smaller volumes. The apparatus is simple, inexpensive, and dependable. Accuracies in the order of 2% have been demonstrated (see Table I). The technique is even easier to use than the conventional macro method.

TABLE I

SUMMARY OF MOLECULAR WEIGHT DETERMINATIONS

| *Compound* | *Molecular weights* | | |
|---|---|---|---|
| | *calculated* | *determined* | *% error* |
| 2,2,4,6,6-Pentamethylheptane | 170 | 167 | —1.8 |
| Tetraisobutylene | 224 | 226 | +0.9 |
| *n*-Decane | 142 | 146 | +2.8 |
| Di-*n*-butylphthalate | 278 | 275 | —1.1 |
| Naphthalene | 128 | 127 | —0.8 |
| Phenanthrene | 178 | 178 | 0.0 |
| Benzil | 210 | 208 | —1.0 |

Thermistors have been employed previously in techniques for the determination of molecular weights. NEUMAYER[1] has reported on the use of a 2-thermistor setup for determining molecular weights on the basis of differences in temperatures of a solution and its solvent in contact with the solvent vapors. DIMBAT AND STROSS[2] have reported on a thermistor ebulliometer. The technique reported in this article employs a single thermistor to detect the steady state freezing point difference between a solvent and its solution of the material whose molecular weight is to be determined. A Wheatstone bridge circuit is used to detect the change in resistance of the thermistor with temperature. The cooling curve and steady state freezing point are recorded on a strip chart recorder. Benzene, a very satisfactory solvent for determining molecular weights of hydrocarbons in the molecular weight range 200 to 600, was used as the solvent for this work[3].

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* This work was supported in part by the U. S. Atomic Energy Commission, Division of Research, Contract No. AT (40-1)-2490.

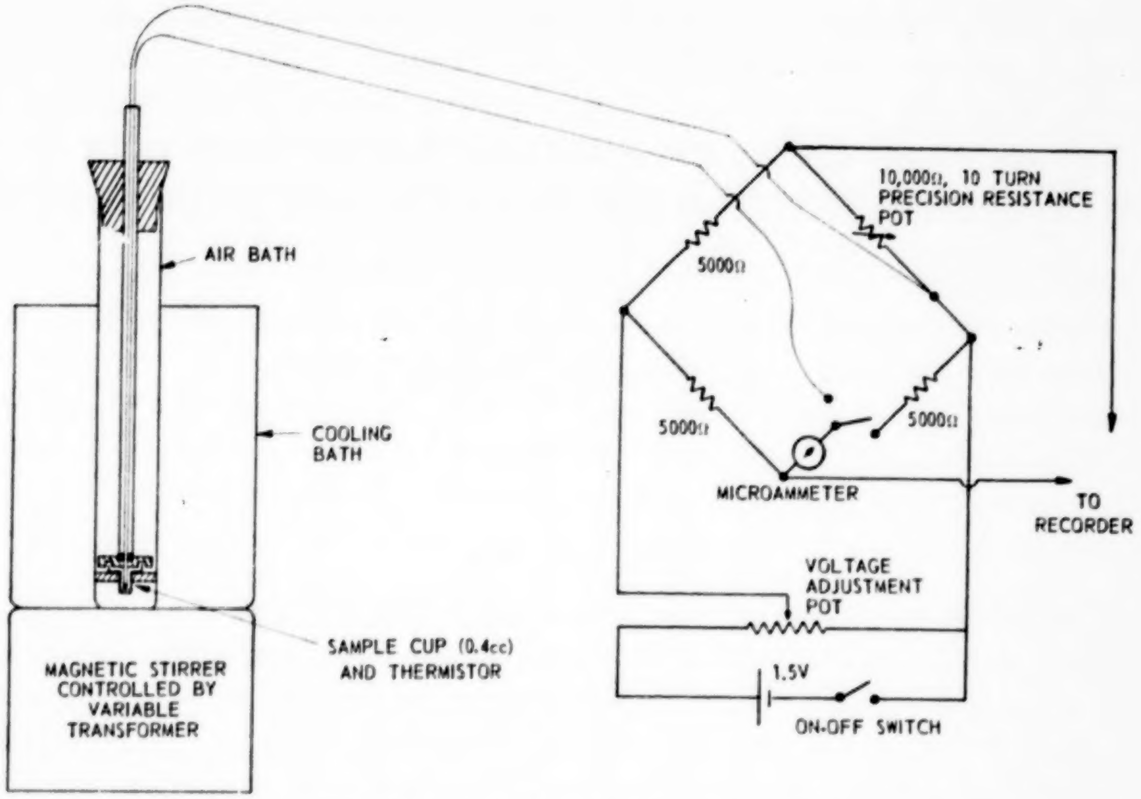
AIR BATH
COOLING BATH
SAMPLE CUP (0.4cc) AND THERMISTOR
MAGNETIC STIRRER CONTROLLED BY VARIABLE TRANSFORMER
10,000Ω, 10 TURN PRECISION RESISTANCE POT
5000Ω
5000Ω
5000Ω
MICROAMMETER
TO RECORDER
VOLTAGE ADJUSTMENT POT
1.5V
ON-OFF SWITCH

Fig. 1. Apparatus for molecular weight determination, with associated circuitry.

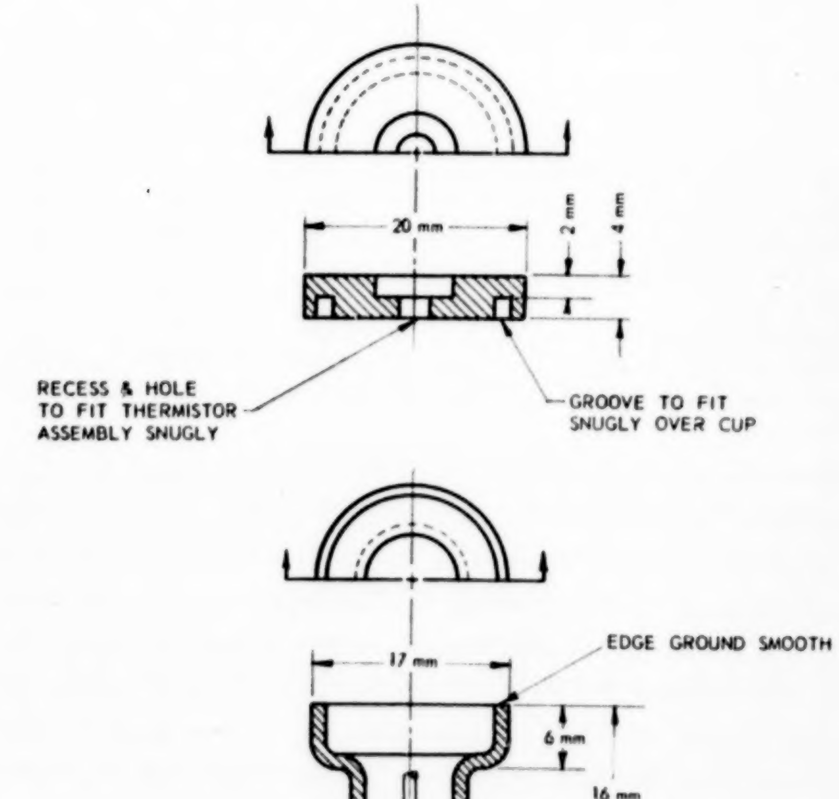
20 mm
2 mm
4 mm
RECESS & HOLE TO FIT THERMISTOR ASSEMBLY SNUGLY
GROOVE TO FIT SNUGLY OVER CUP
EDGE GROUND SMOOTH
17 mm
6 mm
16 mm
1 mm WALL TH.
CUP TO BE LOCATED APPROXIMATELY 4 mm FROM BOTTOM OF AIR BATH
10 mm
THERMISTOR TO BE LOCATED APPROXIMATELY AS SHOWN

Fig. 2. Sample cell and cover plate.

## APPARATUS

The apparatus with the bridge circuitry is shown in Fig. 1. For the studies reported in this paper, a water and ice mixture in a 1000-ml beaker was adequate as a constant temperature bath. The dimensions of the air bath surrounding the sample holder were selected to give the proper cooling rate of the sample. Stirring of the ice bath is necessary to produce a uniform bath temperature. For solvents other than benzene, a regulated bath could be used to provide a temperature several degrees below the freezing point. A high degree of regulation would be required due to the sensitivity of the thermistor. A magnetic stirrer is used to stir the sample by a small nickel-plated stirring bar in the sample holder.

The thermistor element used in this work was a VECO 32A84, manufactured by the Victory Engineering Corporation, Union, New Jersey. At 25° this thermistor has a resistance of 2000 ± 400 ohms and a negative temperature coefficient of resistance (—3.9%/°C). Its resistance at the freezing point of benzene is approximately 5000 ohms. It is necessary that the thermistor be positioned as shown in Fig. 2, which gives details of sample cell and coverplate.

## EXPERIMENTAL

### *Adjustment of the apparatus*

The range and the position of the freezing points of the solvent and a solution on the recorder chart may be varied by varying the voltage to the bridge and the setting of the 10-turn precision resistance pot. Additional adjustment is available with a multi-range recorder. The bridge voltage must be low to prevent excessive heating of the thermistor. The apparatus is adjusted for a large recorder deflection in the range of molal concentration being studied. This is accomplished by a series of trial and error experiments. A small amount of experience will allow the rapid selection of a suitable range.

### *Standardization of the voltage supply*

The recorder range is adjusted as described above. A constant resistance is switched in for the thermistor. The readings of the precision resistance pot and an ammeter, which is located in the thermistor arm of the bridge, are noted. The voltage may hereafter be standardized by reproducing the readings of the pot and ammeter.

### *Calibration and molecular weight determinations*

The procedure for determining the steady state freezing point of a solvent or a solution follows. The stirring bar and a small amount of desiccant, such as finely divided magnesium sulfate, are placed in the cell. The cell is then inserted in the air bath and seated in a cork ring. The liquid is then pipetted into the cell to the level of the shoulder. The sample cell coverplate and the thermistor probe assembly are then quickly put in place. The air bath is lowered into the ice water bath so that it touches the bottom of the beaker. Stirring is started immediately and the stirring rate is adjusted to the maximum value not producing a vortex. When the recorder pen comes on scale, the chart is started and the cooling curve is drawn by the recorder. The sample is allowed to continue to cool until freezing occurs. This is indicated by a rapid rise of the recorder pen from the supercooling region to a peak which corresponds to the steady state freezing point. The peak for pure benzene is a flat plateau with a duration of one and a half minutes. Solutions exhibit a shorter plateau, the length decreasing with increasing concentration. Fig. 3 shows typical cooling curves. In this work, a 5-mV recorder setting was used; part of the supercooling region was off scale.

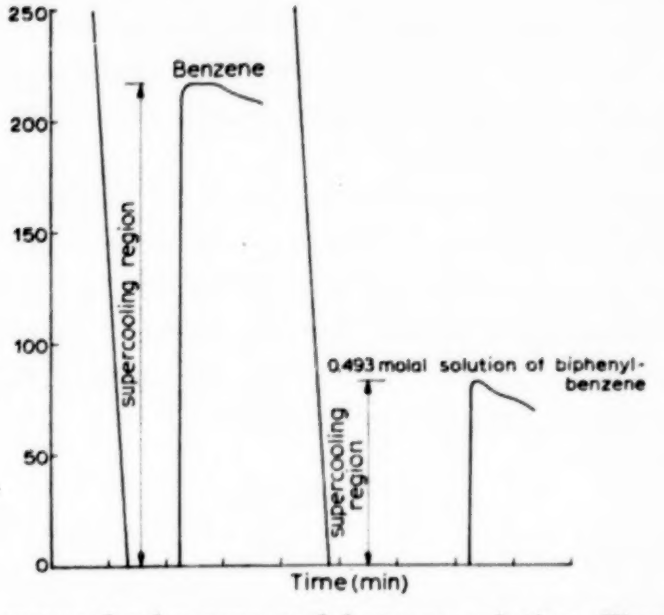

Fig. 3. Typical cooling curves for benzene and benzene solution. Thermistor current: 95 $\mu$A; precision resistance pot setting: 5190 $\Omega$; recorder range 5 mV.

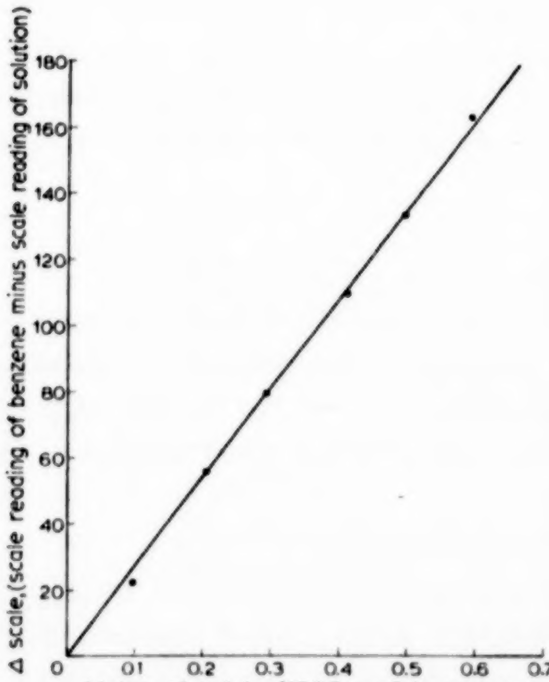

Fig. 4. Typical calibration curve with known solutions of biphenyl in benzene. Thermistor current, 95 $\mu$A; precision resistance pot, 5190 $\Omega$; recorder range, 5 mV.

Since this technique employs the steady state freezing point method, it is necessary to calibrate the apparatus with solutions of benzene and a material of known molecular weight. For this work, biphenyl was chosen as the standard material. The steady state freezing points for benzene and a number of solutions of biphenyl in benzene were determined as described above, and the chart was calibrated directly in molal concentration units. The calibration curve is shown in Fig. 4. Since the variation of the resistance of the thermistor with temperature is not linear, it might seem that the calibration curve should also be non-linear. However, since the temperature range over which the thermistor operates is small (approximately 0.4°), the calibration curve is linear within experimental accuracy. Calibration can be simply accomplished by determining the cooling curves for benzene and one solution. It is desirable to recalibrate from day to day as characteristics of thermistors may drift slightly. The apparatus should be allowed to warm up. Recalibrations should be performed for changes in batches of solvent or for any change in the precision resistance pot setting.

The procedure for determining molecular weights follows. The difference between the scale readings for freezing points of benzene and a solution of the unknown in benzene is obtained. The molal concentration is read on the calibration curve. The molecular weight is calculated from weights of the solvent and unknown.

The molecular weights of a number of known compounds were determined as described above and the results compared with the calculated values. These results are summarized in Table I.

## SUMMARY

An apparatus for extending the steady state freezing point depression method to small volumes, of the order of 0.3 or 0.4 ml, has been developed. A thermistor is used as the temperature sensing element, in one arm of a Wheatstone bridge. The apparatus is simple and dependable. Accuracies in the order of 2% are easily attainable.

## RÉSUMÉ

Des semi-microdéterminations cryoscopiques de poids moléculaires ont été effectuées à l'aide d'un "Thermistor", permettant ainsi des mesures sur des volumes de 0.3 à 0.4 ml.

## ZUSAMMENFASSUNG

Beschreibung einer kryoskopischen Methode zur Molekulargewichtsbestimmung unter Verwendung von Thermistoren.

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# DIFFERENTIAL PRECIPITATION IONOGRAPHY FOR QUALITATIVE CATION ANALYSIS*

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(Received February 7th, 1961)

## INTRODUCTION

It is frequently desirable to have a rapid method of detecting the presence of certain metallic ions in a chemical specimen. In various studies of air pollution, industrial hygiene, and metal analysis the necessity of dissolving dusts and small portions of solid samples to perform wet chemical tests can be tedious and time-consuming.

Various investigators have described methods of overcoming these difficulties. Spectrographic methods are capable of detecting or determining numerous metals in the same sample, as exemplified by their use by the National Air Sampling Network of the U.S. Public Health Service[1]. However, the cost of a suitable spectrograph limits the use of the procedure. The ring-oven technique of WEISZ[2] can be used to separate minute quantities of solutions containing many ions. The electrophoretic methods used by KIRK *et al.*[3] on cellulose acetate membranes takes advantage of the properties of these membranes to study limited amounts of materials. Precipitation chromatography has been used to detect metals as they diffuse into an agar gel column[4]. This paper describes a method of rapidly identifying certain metal ions in this important microgram range in one or two simple operations.

## DEVELOPMENT OF METHOD

Some adaptation of an ion migration technique seemed desirable as a method of cation analysis. In the course of experimentation, a method was discovered which appears to depend not upon relative migration speed, but upon the pH at which precipitation of the metal hydroxide occurs. Gels were investigated as substrates, but were too seriously deformed by heating at the electrodes to be useful. Membrane filters proved to be a desirable substrate in this case (Millipore Filter Corporation, Bedford, Mass.). Heavy gauge platinum wire was chosen for the electrodes as the material least likely to be affected by surface changes.

A dependable method of holding the sample and applying the current was necessary. A device was built on a triangular base which could be leveled by means of three adjustable screws. This base supported the electrode clamps which were variable in separation and were controlled by set screws. The electrodes, of 24-gauge platinum wire or 1/8-in. diameter rods, made contact with the substrate on a microscope slide supported directly below the electrode holder. A small leveling bubble attached to

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* This work was supported by Grant No. S-12(C4) from the Bureau of State Services, U.S. Public Health Service.

the base directly back of the sample area facilitated exact adjustment. Power was obtained from a 0–50 V D.C. power supply A mA-meter was included in the circuit (Fig. 1).

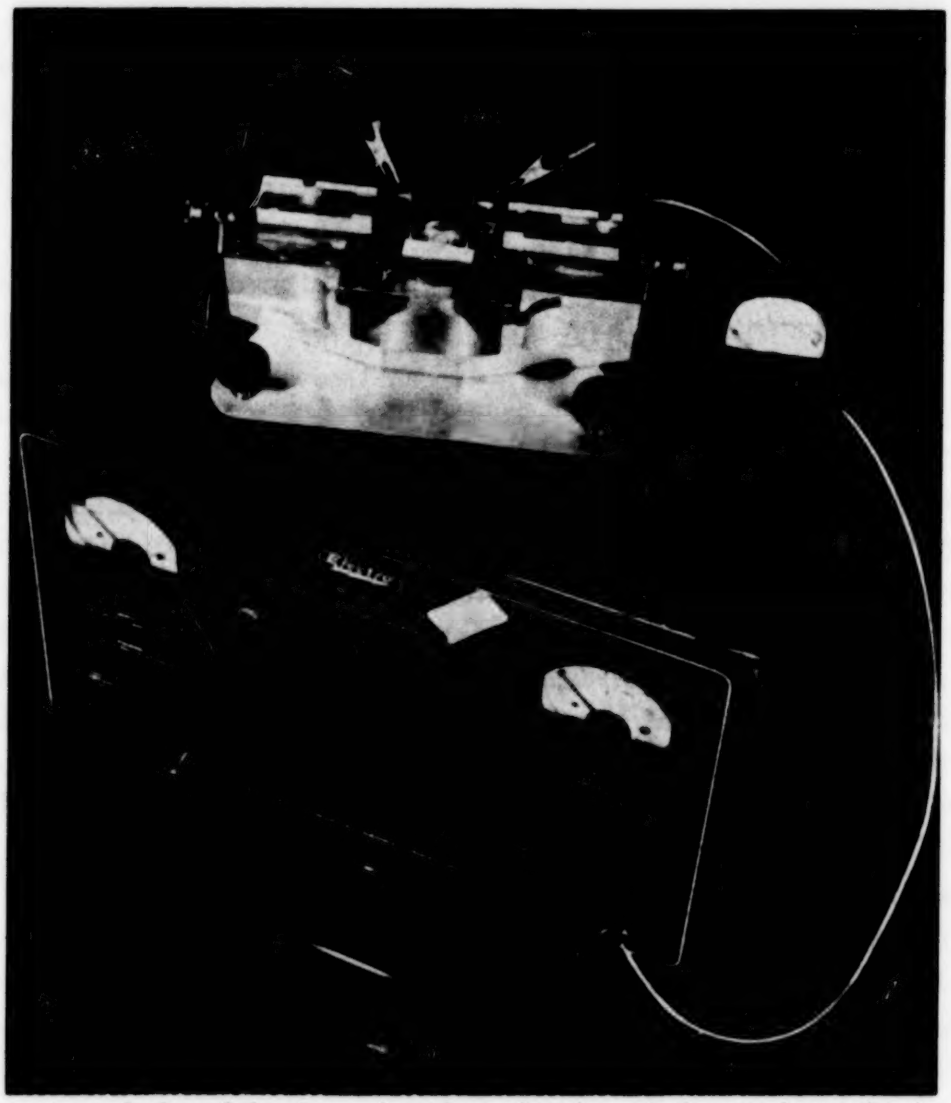

Fig. 1. Instrument as designed for ion migration, showing platinum electrodes in contact with filter strip.

In order to provide electrolyte to conduct the current, a small piece of blotting paper on a microscope slide is soaked with a sodium chloride–hydrochloric acid solution. A small strip of membrane filter (30 mm by 5 mm is a suitable size) is placed on the wet blotter and allowed to take up the electrolyte. The sample is placed on the center of the filter with a needle or the shaped end of a toothpick. If the material is soluble, current is applied. For insoluble dusts pre-treatment in hot acid fumes may be necessary; 1 h at 50° is usually sufficient. Ideally, the potential applied moves the cations toward the negative pole. Simultaneously, electrolysis of sodium chloride liberates sodium hydroxide at the negative pole causing a pH gradient around the electrode. When the cations reach a point which corresponds to their precipitation pH they cease to migrate.

When migration is complete the filter is removed from the electrode holder and placed on a few drops of a suitable reagent (Table II) on a clean slide. It is examined microscopically with transmitted light at low magnification. Colored precipitates in circles or semicircles around the area of the negative pole will indicate the presence of the cations for which the test was made (Fig. 2). The precipitates diffuse rapidly and as the filter dries, the color may change, so that for best results the sample should be examined at once. Rapid diffusion may be partially prevented by "fixing" the sample with a clear plastic spray, such as Krylon. When the plasticized filter has dried, it may be mounted with immersion oil in the usual fashion. This changes the appearance of colored precipitates somewhat, and care must be used in interpretation.

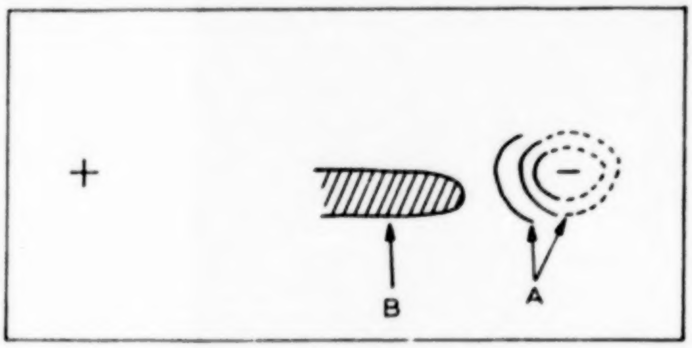

Fig. 2. Diagram showing ion separation after migration. A, Area of clearly separated bands partially or completely circling negative pole. B, Area of poor separation caused by slow moving ions such as iron(III), resulting in indistinct outline.

In the case of extremely refractory metal dusts or solid samples of metals, the sampling method of STEPHEN[5] was adapted. For the first part of the test the platinum electrodes were replaced with an aluminum electrode at the negative pole and one of stainless steel turned to a point as he describes at the positive pole. The movable electrode holders are adjusted for the size of the sample and the wet filter placed on the sample in such a way that the aluminum electrode touches the sample. If the sample is a dust it is put on a slide in a small pile; the filter and aluminum electrode covers one edge of the pile and the stainless steel electrode is thrust into the remainder of the pile. Current is passed as STEPHEN describes. A small amount of sample is deposited on the filter by anodic dissolution. This method of obtaining a soluble sample is applicable to a number of types of analysis and is particularly amenable to analysis by the migration methods described above. The entire process may be completed in 10 min.

A series of tests was made to determine the best separation of the ion bands (Table I). The amount of electrolyte used was kept constant by using a piece of blotting paper sufficiently large to be saturated, with only a slight excess, by the quantity of electrolyte. The electrolyte is delivered from a calibrated dropper. For these tests, 1 ml was used. As can be seen from Table I, the strength of the electrolyte is not critical over a fairly large range.

TABLE I

EFFECT OF ELECTROLYTE COMPOSITION ON SEPARATION

| *Electrolyte* | | | *Potential gradient* | | | *Results after reaction* |
|---|---|---|---|---|---|---|
| *$H_2O$ (ml)* | *Conc. acid (drops)* | *NaCl (mg)* | *V* | *min* | *mA* | |
| 5 | 1 drop HCl | 6 | 20 | 2 | 20 | no migration |
| 5 | 1 drop HCl | 15 | 20 | 2 | 20 | diffuse ppt., poor separation |
| 5 | 1 drop HCl | 20 | 20 | 2 | 20 | complete migration, good separation |
| 5 | 1 drop HCl | 30 | 20 | 2 | 20 | complete migration, good separation |
| 5 | 2 drop HCl | 30 | 20 | 2 | 30 | very large "blister" at neg. pole |
| 10 | 1 drop HCl | 30 | 20 | 3 | 20 | requires long time for poor separation |
| 5 | 1 drop HCl | 60 | 20 | 2 | ? | chlorine given off |
| 5 | 1 drop $HNO_3$ | 16[a] | 20 | 2 | 50 | slow movement |
| 5 | 1 drop $HNO_3$ | 16[a] | 50 | 2 | 80 | good separation, much heat and boiling |

[a] $NaNO_3$ instead of NaCl.

A series of tests was made to determine the optimum potential gradient. Electrode separations of 12 mm, 15 mm, and 24 mm were used. A separation of 15 mm seems to give the most consistent results. At this electrode separation, 20 V gives an ammeter reading of approximately 18 mA. This is somewhat interdependent with the strength of the electrolyte. At a 15-mm electrode separation and 20 V, 18 mA, migration is fairly complete for all but the slowest ions, *i.e.*, iron(III), after 1.5 to 2 min. Considerable heat is generated at the negative pole which manifests itself in "blistering" of excess electrolyte at the negative pole and violent bubbling. To reduce the heat, a 100-Ohm resistor may be added to the circuit in parallel with the sample substrate. At 20 V the current drops to 4 mA and the bubbling is correspondingly decreased. Migration and separation of ions seems to be unimpaired except for those ions whose migration rate is slow.

The type of reagent used depends on the nature of the sample. A saturated solution of rubeanic acid in 50% aqueous methyl alcohol will determine the presence of iron, copper, nickel and cobalt in a single sample by the formation of yellow, green, blue, and pink precipitates, respectively. Some care is needed in interpretation, as small amounts of nickel give a pinkish-purple color which may be confused with cobalt. Other general reagents such as 10% aqueous potassium ferrocyanide, and benzidine in acetic acid, may be used to determine the presence or absence of groups of cations. In many cases if the first reagent gives a slight precipitate, excess reagent may be blotted away and a second or even a third applied to the same filter. Up to four ions have been identified in a single test. Where an extremely heavy precipitate occurs due to large amounts of one cation, it will be necessary to prepare one or more fresh samples to confirm the presence of trace amounts of other ions. Confirmatory tests may be made by using sensitive spot test reagents, such as are described by FEIGL[6]. A reagent which gives a white or pale yellow precipitate is not satisfactory unless the filter is to be made transparent and viewed with transmitted light.

## DISCUSSION

The most probable explanation for the formation of circles or semicircles around the negative pole is the establishment of a pH gradient by the electrolysis of sodium chloride and the diffusion of the resulting base into the substrate. The cations of the sample will migrate under the potential gradient until their characteristic precipitation pH is reached. At this point they will precipitate as the appropriate oxide or hydroxide. Since the migrating ions will follow the lines of force, whether they ultimately precipitate as arcs, semicircles, or complete circles will depend on the initial location of the sample on the filter and on the geometry of the filter and the electrodes.

Other characteristics of the migration which lend support to the theory of the precipitation mechanism are the precipitation of the cations in the order of their precipitation pH and band width independent of time of migration. No matter where the original sample is placed on the filter, as long as it is outside the area of pH gradient, the final band of precipitated material will be in the pH gradient area, in some fraction of a circle, independent of the shape of the original sample. This also suggests that the mechanism is other than ionophoresis, and is in addition an advantage when sampling particulate matter or sampling by anodic dissolution.

The technique has been applied to several different types of samples (Table II). Dusts, collected in bulk and deposited on the filter, or collected on the membrane

## TABLE II

### RESULTS WITH SAMPLES

| *Sample* | *Pretreatment* | *Reagent* | *Ions found* | *Ions known to be present* |
|---|---|---|---|---|
| Dust prepared in lab | — | rubeanic acid | iron, nickel | iron, nickel, as chlorides |
| Dust prepared in lab | — | rubeanic acid and sodium rhodizonate | iron, nickel, copper, lead | iron, nickel, copper and lead as soluble salts |
| Dust prepared in lab | 1 h in HCl vapor | rubeanic acid | iron, copper | iron, copper, nickel as oxides |
| Scrapings from iron meteorite | 1 h in HCl vapor | rubeanic acid | iron, nickel | iron, nickel, cobalt |
| Scrapings from iron meteorite | anodic dissolution | rubeanic acid | iron, nickel, cobalt | iron, nickel, cobalt |
| Magnetic dust from roof | anodic dissolution | potassium ferrocyanide | iron, copper | unknown |
| Magnetic fly ash | anodic dissolution | potassium ferrocyanide | none[a] | unknown |
| Nickel, U.S. coin | anodic dissolution | rubeanic acid | copper, nickel | copper, nickel |
| Dime, U.S. coin[b] | anodic dissolution | rubeanic acid | silver, copper | silver, copper |
| Nichrome wire | anodic dissolution | rubeanic acid | nickel, iron | nickel, iron, chromium, manganese[c] |
| Ore from Tahawus Mine, N.Y. | anodic dissolution | 1. potassium ferrocyanide<br>2. hydrogen peroxyde | iron | iron, titanium |

[a] In the microscope, a few individual blue areas were seen, indicating iron. No circles.

[b] When silver is present with NaCl–HCl electrolyte, it is precipitated as AgCl at the point of contact and separates without migration.

[c] No tests were made for chromium and manganese.

filter itself, migrate most easily in soluble form. If anodic dissolution as described above is not possible, it is necessary to treat the filter with acid fumes as previously mentioned. Metals such as coins, foil, alloys, etc., yield readily to treatment. The tests with ores show that the sample must be clamped or held in such a way that a flat face is in firm contact with the electrode. The ore must also have a high percentage of metal on the surface and in sufficiently continuous amounts that both electrodes touch the same area. Earthy or low grade ores do not respond.

Great care must be taken with interpretation. The colors of the reaction precipitates are subject to diffusion and fading as the filter dries. Varying amounts of material may give changes in shades of color. The reagent should always be allowed to soak up through the membrane filter as described above, to avoid washing away the reaction product. Test samples should be made with knowns until the operator is completely familiar with the behavior of the ions. The tests are not quantitative. However, an experienced technician can arrive at a fairly precise estimate of the amounts present by comparing color, amount of precipitate, and general appearance. The technique is primarily designed for rapid qualitative work, as it is not as sensitive as some spot test techniques. It should be emphasized that the amounts of material required are sufficiently small that in many cases the method is essentially non-destructive testing. Estimates can be made well into the $10^{-6}$–$10^{-9}$ g range depending on how the original sample was collected. The method should be readily applicable to qualitative examination of industrial dusts, metals testing and similar areas of interest.

### ACKNOWLEDGEMENTS

F. HUNEMULLER, student technician, assisted in preparing samples for these experiments. E. A. NEIL aided in designing the instrument. This assistance is gratefully acknowledged.

### SUMMARY

A method — differential precipitation ionography — is described for the separation and detection of cations in mixtures in trace amounts. The ions are caused to migrate by application of current to a supporting membrane. The substrate is kept moist with an electrolyte so chosen that its electrolysis provides a pH gradient. The migrating ions form narrow bands of their oxides or hydroxides at the point of their precipitation pH in this field. After this separation the filter is developed with a suitable reagent and examined microscopically. Several metal ions can be detected in a single sample. Materials in amounts as low as $10^{-9}$ g may be detected.

### RÉSUMÉ

Une méthode rapide, par ionographie à précipitation différentielle, a été mise au point pour la séparation et l'identification de cations à l'état de traces (jusqu'à $10^{-9}$ g). Après séparation, le filtre est traité par un réactif approprié et examiné au microscope.

### ZUSAMMENFASSUNG

Beschreibung einer raschen Methode zur Trennung und zum Nachweis von Kationen in Spurenmengen durch differentielle Fällung auf einer mit einem geeigneten Elektrolyten getränkten Membran, an die eine Spannung angelegt wird; dies führt zur Bildung eines pH Gefälles. Die an den entsprechenden pH Stellen gebildeten Niederschläge werden mit geeigneten Reagenzien behandelt und die entstandenen Niederschläge mikroskopisch untersucht.

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# ORGANIC COMPOSITION ANALYSIS BY COMBINATION OF GAS CHROMATOGRAPHY WITH INFRARED SPECTROPHOTOMETRY

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(Received January 17th, 1961)

As a result of the rapid development and increasing complexity of industrial chemical technology, the demands made on the analytical chemist have increased from the standpoints of time, precision and selectivity. This is particularly true in the petroleum and other organic chemical industries where complicated mixtures of related compounds have become an everyday problem. Lacking the desired selectivity in most cases, the analysis of these complicated organic mixtures becomes a case of separation, identification and determination.

One approach to solving this problem has been through the combination of gas chromatography with infrared spectrophotometry. Barring preparative scale work, the samples charged to the gas chromatographic unit are usually the order of microliters. The separation, trapping, and identification of a component from this size charge becomes a significant problem. SZYMANSKI[1] approached the problem by placing an activated surface material on rock salt and trapping the species by adsorption. An infrared spectrum of the adsorbed species was then obtained. A number of other workers, including DOERING AND BUTTERY[2], BELLIS AND SLOWINSKI[3], and CRAIG *et al.*[4] have attempted to trap the samples as liquids via cold trap techniques. Another approach, that of trapping as a gas, has been the topic of papers by WHITE *et al.*[5], STEWART *et al.*[6], and ANDERSON AND DUNCAN[7].

In this paper a technique for trapping and obtaining infrared spectra in the gas phase is presented and some of its potentialities are discussed.

## EXPERIMENTAL

### *Apparatus*

A Fisher-Gulf Partitioner was used for the gas chromatography work. The outlet for the gas chromatographic effluent was connected to a Republic four-way reversing valve, #310-6. The Perkin-Elmer minimum volume gas cell was connected across the valve using 1/8 in. copper tubing for lines. Two Hoke valves were connected into the system to provide a quick flushing arrangement. The cell and lines were wrapped and heated with thermocouple wire. The spectra were run on a Perkin-Elmer 221 spectrophotometer.

### *Reagents*

(*1*) The *n*-butanol, *sec*-butanol and *tert*-butanol were obtained from the Eastman Kodak Company.

(2) The hexene-1, heptene-1 and octane-1 were Phillips Petroleum Company pure grade reagents (99 mol % minimum).

### *Mode of operation*

A schematic diagram of the apparatus is given in Fig. 1. The trapping arrangement is best illustrated by tracing the flow of the carrier gas through the system. The carrier gas passes through the reference side of the thermal conductivity cell, picks up the sample and enters the column. The effluent from the column passes back through the thermal conductivity cell and into a Republic four-way reversing valve. When the Republic valve is in position A, the gas flows through the minimum volume gas cell whereas in position B it is vented to the atmosphere and the gas cell sealed off.

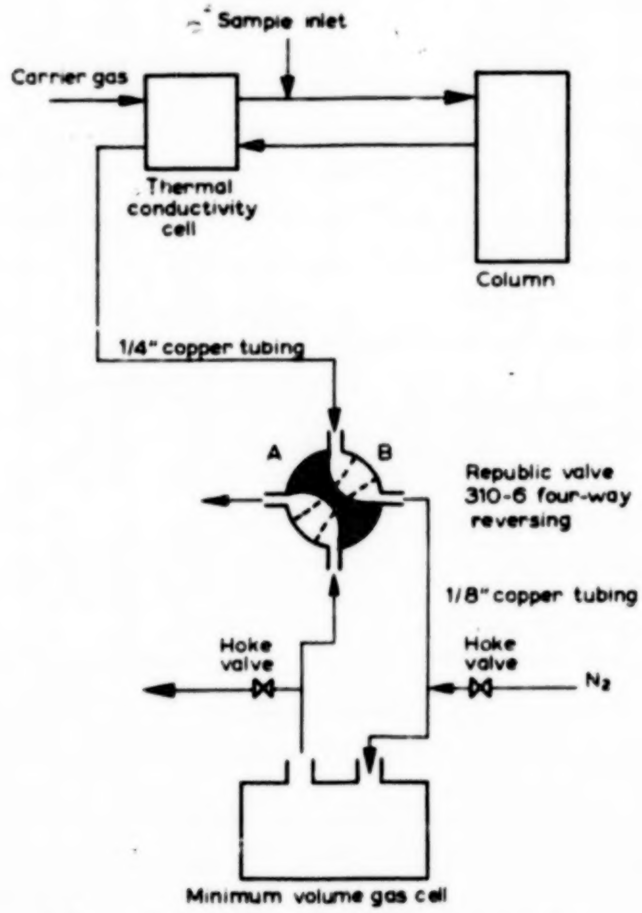
Sample inlet
Carrier gas
Thermal conductivity cell
Column
1/4" copper tubing
A
B
Republic valve 310-6 four-way reversing
1/8" copper tubing
Hoke valve
Hoke valve
N₂
Minimum volume gas cell

Fig. 1. Schematic diagram of apparatus.

In order to trap a sample, the minimum volume gas cell was positioned in the spectrophotometer and the instrument set on a characteristic vibration of the component in question, generally a carbon–hydrogen stretching frequency. The buildup of a component in the gas cell was monitored and the cell sealed off when maximum absorption was reached. The infrared spectrum was then run under the desired conditions. Flushing was accomplished by opening the two Hoke valves and passing a stream of dry nitrogen through the cell. The Hoke valves were then closed and the Republic valve opened to trap another component.

In general, one component was trapped for each charge to the gas chromatograph. However, where fast scans were applicable, *i.e.*, 4 min, it was possible to trap consecutive components if they were separated by 6 min in retention time.

*Sensitivity*

An important point concerning an apparatus of this type is the amount of sample that must be charged to the gas chromatograph in order to obtain a useful infrared spectrum for the trapped component. This sensitivity is a function of the specific absorptivities of the compound and the maximum concentration that may be attained in the gas cell.

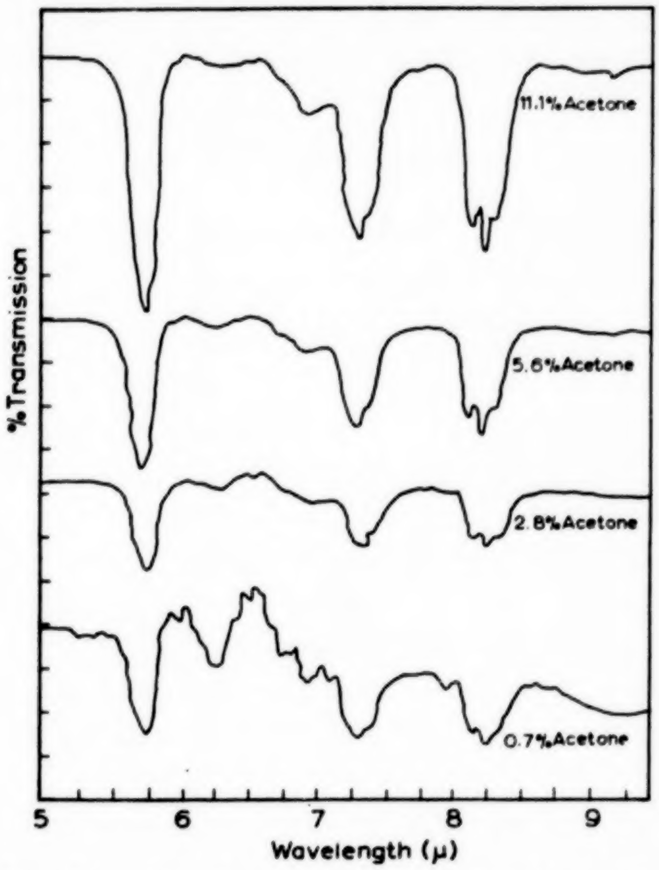

Fig. 2. Infrared spectra of trapped acetone fractions. 20-μl charges.

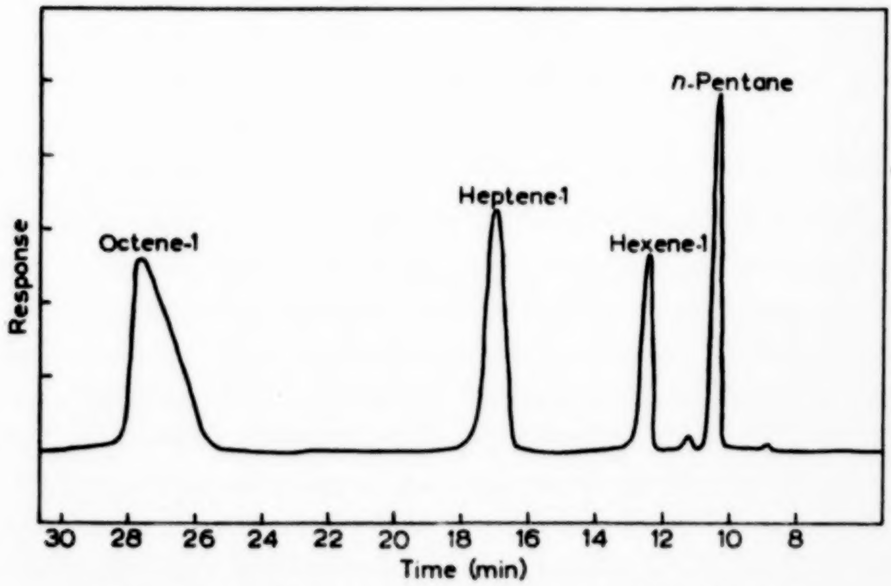

Fig. 3. Gas chromatography trace of alkene blend.

An experimental investigation of the sensitivity aspect was made using acetone as the component to be trapped. Blends of acetone and *n*-butanol were prepared, separated on the gas chromatograph, the acetone trapped, and its spectrum recorded. A selected portion of the spectra obtained for the various blends is shown in Fig. 2. Based upon these data, acetone can be trapped and identified if it is present as 0.1 to 0.2 µl by volume in the charged sample. A comparison of specific absorptivities with that for acetone will give a rough approximation of the amount of component needed for identification using the same technique. In investigating these acetone blends, 5X scale expansion was used at the 0.7% level. The over-all sensitivity attainable depends upon the scale expansion features available on the spectrophotometer.

*Separation of blends*

In order to illustrate the potentialities of this technique, we prepared two blends — one an alcohol blend and the other an alkene blend — for separation and determination. The alkene blend consisted of hexene-1, heptene-1, and octene-1 with *n*-pentane added as a retention time standard. The gas chromatographic trace of this alkene blend is shown in Fig. 3. Using 50-µl charges to the gas chromatograph, each of the major alkene components was trapped and the infrared spectrum recorded. The spectra are shown in Fig. 4. From these spectra it is easy to ascertain that each compound is an unsaturate; this is evidenced by the ethylene carbon–hydrogen stretch at 3.25 µ and the C=C stretch at 6.1 µ. Furthermore, it is also evident that each compound has terminal unsaturation as evidenced by the fingerprint structure at 10.1 µ and 11 µ.

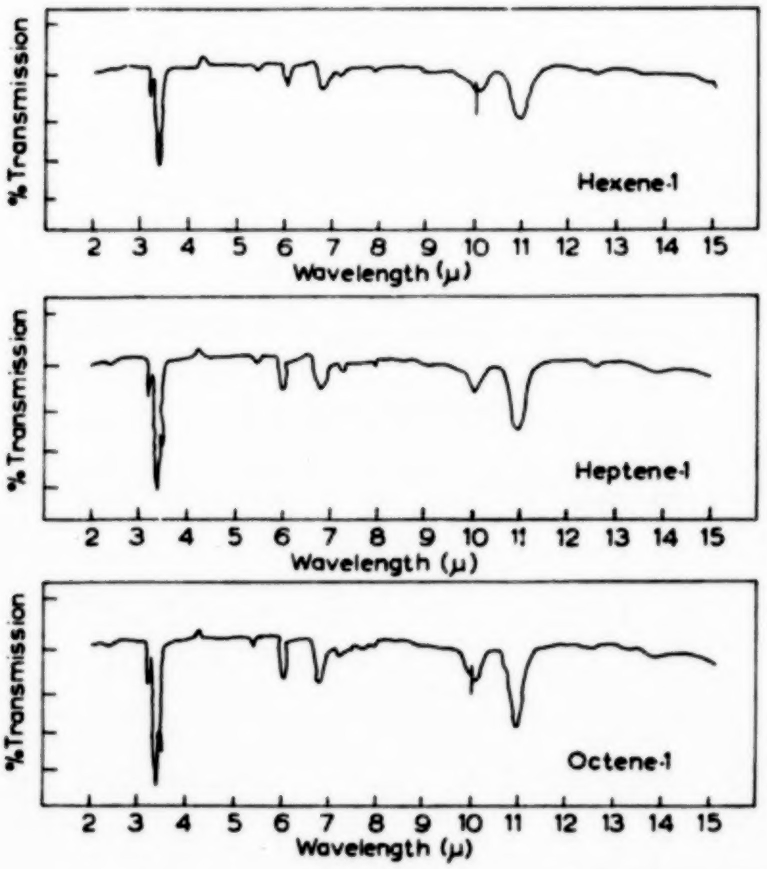

Fig. 4. Infrared spectra of resolved alkene blend.

As another example, a blend consisting of *t*-butyl alcohol, *sec*-butyl alcohol, and *n*-butyl alcohol was prepared. Using 50-µl charges to the gas chromatograph, the compounds were separated, trapped, and their spectra recorded. The gas chromatographic trace of the alcohol blend is shown in Fig. 5. The clarity of the spectra obtained (Fig. 6) should be pointed out with respect to the free OH stretching vibration at approximately 2.7 μ and the normal alcohol fingerprint region (8.0–9.5 μ) in which differentiation as to types can be very easily seen.

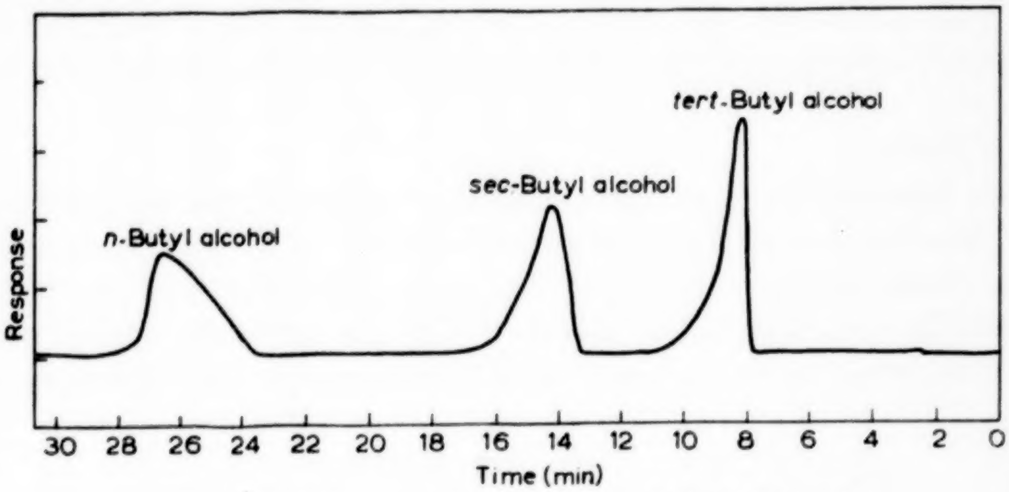

Fig. 5. Gas chromatography trace of alcohol blend.

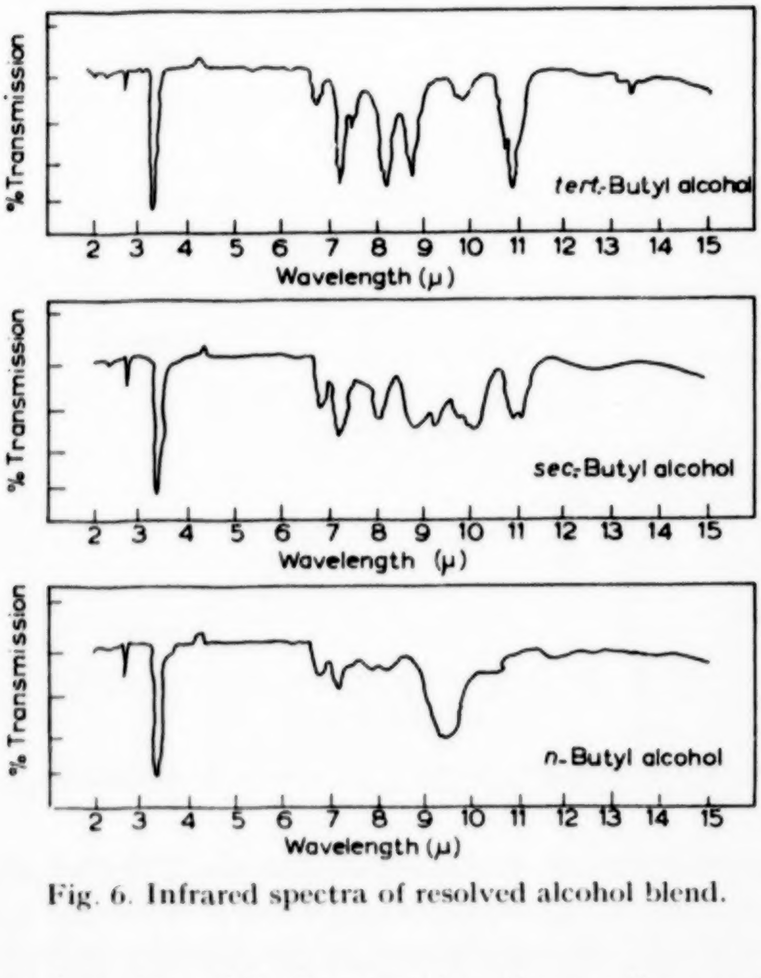

Fig. 6. Infrared spectra of resolved alcohol blend.

These data, in conjunction with the retention times, allow positive identification of the compounds. Once identity has been established, quantitative data may be calculated using the proper calibration curves and the peak area of the component.

The spectra obtained on these blends were run using 1/4 scale expansion and automatic suppression. Time required per scan was approximately 4 min.

## DISCUSSION

The basic data provided by this technique are retention time, infrared spectrum and peak area. The combination of retention time and the infrared spectrum usually suffices to identify the component. From proper calibration curves the peak area can be used to secure quantitative data. Thus, a complicated organic mixture can be analyzed qualitatively and quantitatively in a very short time.

Applications of this technique have been made in three areas to date. First, it has been used to analyze mixtures from exploratory organic reactions. Secondly, it was applied in producing pure compounds in order to obtain reference spectra. Thirdly, it has been used in determining composition in process streams in order to facilitate gas chromatographic calibration procedures. These applications are but a few of the many possible through the use of combination techniques.

## ACKNOWLEDGEMENT

The authors wish to thank Esso Standard, Division of Humble Oil & Refining Company for permission to publish this work.

## SUMMARY

A technique combining gas chromatography with infrared spectrophotometry for analysis of complex organic mixtures has been described and modes of application discussed. The components are trapped and run as gases. Proper use of the data makes possible qualitative and quantitative analysis.

## RÉSUMÉ

Une technique est proposée pour l'analyse de composés organiques, en combinant la chromatographie gazeuse et la spectrophotométrie infra-rouge.

## ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Analyse von Gemischen organischer Substanzen durch kombinierte Anwendung von Gaschromatographie und IR-Spectrophotometrie.

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# THE ABSORPTIOMETRIC DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS

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(Received January 31st, 1961)

## INTRODUCTION

Many procedures have been published for the absorptiometric determination of phosphorus in irons and steels, based mainly on reactions producing either molybdenum blue or vanadomolybdiphosphate for final colour measurement. Many of these procedures have been used in this laboratory, but the need was felt for a fuller understanding of the factors affecting reliability and accuracy. A literature search revealed many conflicting and widely different conditions, and it was decided to investigate the reactions to produce a reliable method for routine work. The vanadomolybdiphosphate reaction was chosen without a final solvent extraction procedure, since this would probably lead to a simpler final method even if subject to some limitation due to some alloying elements.

## EXPERIMENTAL

### *Reagents and apparatus*

All reagents were of "AnalaR" quality where possible. Optical density measurements were made on a Unicam SP. 600 spectrophotometer for the plotting of absorption spectra, and on a "Spekker" absorptiometer using a tungsten lamp and violet No. 601 filters for all subsequent work. This latter instrument was chosen because it was to be used for routine work.

### *Principle of method*

The sample is dissolved in nitric acid and the phosphorus in solution is then oxidised to the reactive orthophosphate state. Addition of vanadate and molybdate then produces the vanadomolybdiphosphate complex, the optical density of which is related to phosphorus concentration.

### *Absorption spectra*

For absorptiometric measurement of the final complex, several wavelengths have been recommended, mainly in the 400–480 m$\mu$ band. It was considered that for routine work, measurements in the ultra-violet region should be avoided, and since simple photo-electric absorptiometers are commonly used in metallurgical analysis, investigations were limited to the near ultra-violet and visible region. By using a combination of methods from the literature, the absorption spectra in Fig. 1 were plotted of iron, reagents, and phosphorus complex. It was found that all absorptions increased rapidly towards the ultra-violet, but Beer's law was sensibly obeyed at wave-lengths between 385–430 mμ. By using the violet No. 601 filters on the "Spekker" absorptiometer, virtually linear calibrations could be obtained.

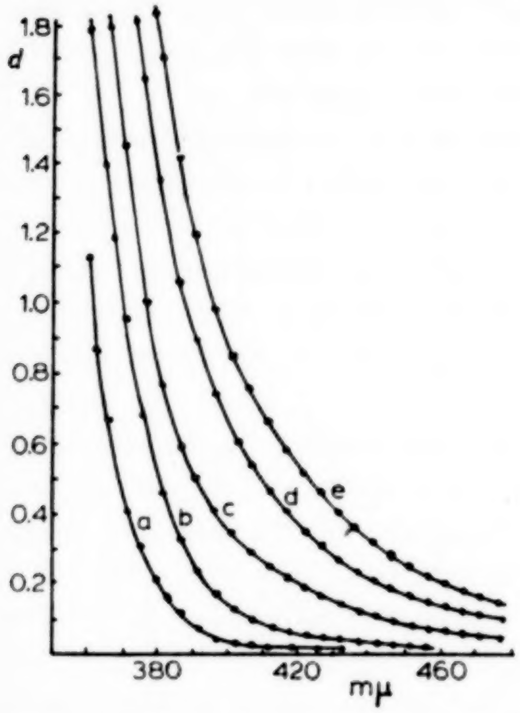

Fig. 1. Absorption spectra. (*a*) Reagents; (*b*) Reagents + 200 mg Fe/l; (*c*) Reagents + 200 mg Fe/l + 3 mg P/l; (*d*) Reagents + 200 mg Fe/l + 9 mg P/l; (*e*) Reagents + 200 mg Fe/l + 12 mg P/l.

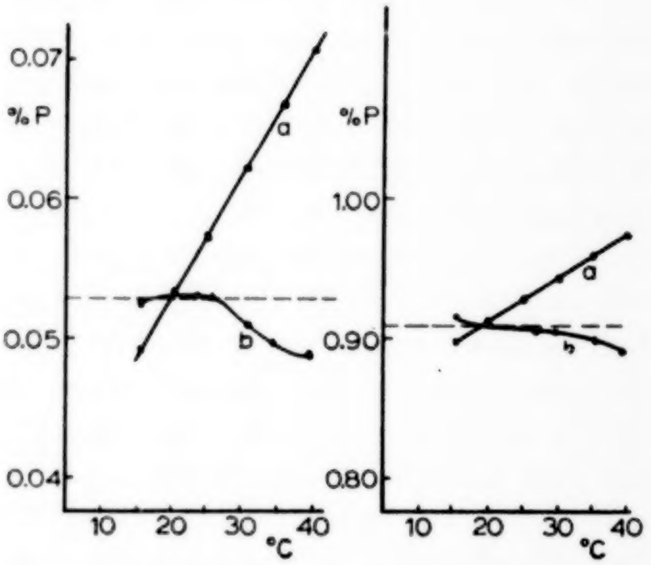

Fig. 2. Temperature compensation. (*a*) not compensated; (*b*) compensated.

*Reaction conditions*

The main factors governing the production of the vanadomolybdiphosphate are the acid, vanadate and molybdate concentrations, and their effects were investigated. Due to the large number of experiments required, a preliminary investigation was made in which acidity and molybdate concentration were varied between 1 and 1.75 $N$ nitric acid and 15–62.5 m$M$ molybdate. With these limits, the effects of variation in vanadate concentration were next investigated as described below. The optimum amount of vanadate required thus established was used in the subsequent investigation of the effects of acidity and molybdate concentration.

*Vanadate concentration*

Sodium vanadate has been proposed[1,2] as reagent in place of the more usual ammonium vanadate because of its greater solubility. However, with the concentrations required for this work, solubility does not present a problem, and ammonium vanadate (available in "AnalaR" quality) was used throughout. Various concentrations of vanadate have been recommended[3–7] *e.g.* 0.4–1.2, 1.7, 2–2.6, and 1–4 when expressed as m$M$ vanadium(V) in the final test solution. In some cases the addition of too large an excess has led to the production of more intense final colours[7–9]. This reaction is often carried out in hot or boiling solution, but times of heating are generally not specified. For these experiments a boiling time of 3 min was used after vanadate addition, although as shown below, reaction in the cold is equally satisfactory.

Varying amounts of ammonium vanadate solution were added to solutions containing both low and high ratios of acid and molybdate. In the test solutions the concentration of phosphorus was 3 mg/l, the phosphorus being omitted from the blank solutions. For both blank and test solutions iron concentrations of 1.5 g and 5 g/l were used. Density readings were taken at timed intervals after the final molybdate addition to observe the rate of development of the final complex.

The total density due to iron, reagents and phosphorus complex increased as the vanadium concentration increased; an increase also occurred in the density of the blank. By using the blank for compensation the density due to the phosphorus complex increased rapidly as the vanadium concentration increased up to 2 m$M$, then between 2–4 m$M$ vanadate the density was virtually constant. With low acid and molybdenum concentrations an excessively long time was required for full colour development, even with up to 4 m$M$ vanadium(V). However, when the molybdate was increased, a rapid development could be obtained with low vanadium concentration, but the time required further increased as the vanadate increased. With high acid and molybdenum concentrations the most rapid colour development occurred within the range 2–4 m$M$ vanadium(V). From the above results it is apparent that the final solution should contain 2–4 m$M$ vanadium(V) for rapid colour development, constant colour intensity and independence from a relatively large variation in iron concentration. By adding 10 ml of 0.35% w/v ammonium vanadate solution for a final 100 ml volume of test solution, the optimum 3 m$M$ concentration is obtained. This addition is not critical to within ± 2 ml.

In many procedures nitric acid is added to the vanadate reagent, although no specific reasons for this are given. Experiments showed that simple aqueous solutions gave identical results to those obtained using acidified solutions, and subsequent work was carried out using the unacidified reagent.

### *Acid and molybdate concentrations*

Nitric acid is probably the most widely used dissolving acid for this determination, although sulphuric[10], hydrochloric[10] and perchloric[7,10] acids have been used. For convenience in routine work on low alloy samples, nitric acid was chosen. Control of acidity is important, since too low a concentration may lead to the formation of precipitates[11,12] or to the formation of yellow vanadomolybdate complexes[3,10]. Too high an acidity may result in slow colour development[1,4,5,9–12] and the production of paler[8] or more intense[1,11] colours, which are often not reproducible. There is a wide variation in recommended acidities from about 0.2 to about 1.6 $N$.

As molybdenum reagent, ammonium molybdate is generally used, with or without the addition of ammonium hydroxide. In preliminary experiments the addition of ammonium hydroxide produced no difference in results and consequently was omitted in later work. The molybdenum concentrations which have been recommended range from the equivalent of about 6 to about 57 m$M$ molybdenum(VI). Experiments were carried out involving 24 combinations of acid and molybdate and both blank and test solutions were treated with each combination. Iron (0.3 g) was present in the solutions (to cover phosphorus ranges for cast iron) and the effect of an increase to 0.5 g for steel analysis is described further below. In the test solutions the phosphorus concentration was 3 mg/l and to determine the rate of colour development, absorption readings were made at timed intervals after adding the molybdate.

For any given molybdenum concentration an increase in acidity produced a decrease in density of both the blank and test solutions. This effect of acidity was more pronounced the lower the molybdenum concentration.

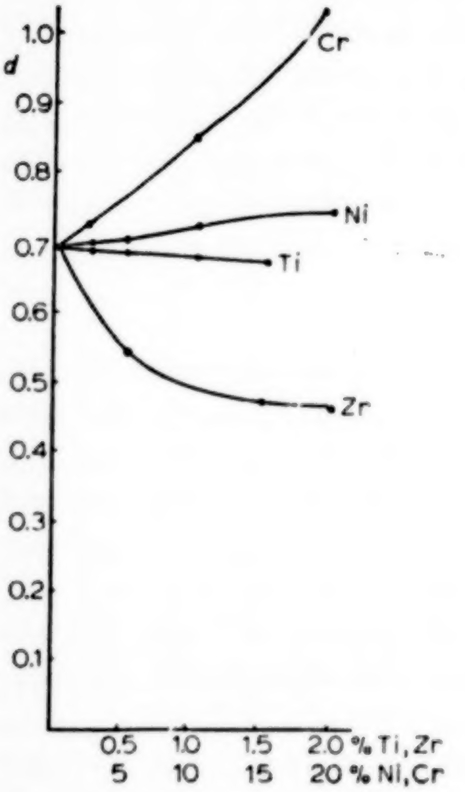

Fig. 3. Effects of Cr, Ni, Ti and Zr. 0.5 g Fe; 0.076% P; 4-cm cells.

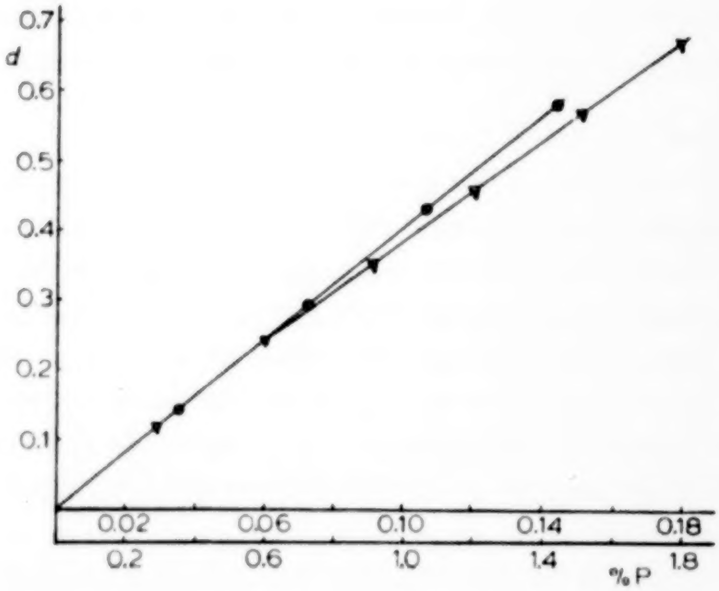

Fig. 4. Calibration curves. ⊙ 0.5-g sample, 4-cm cells; △ 0.3-g sample, 0.5-cm cells.

For any given acidity the blank and test densities increased as molybdate increased, this being more pronounced the higher the acidity. By compensating for the blank absorptions however, the effects of variations in the reagent concentrations upon the colour intensity of the vanadomolybdiphosphoric acid were largely minimised. Thus, the same colour intensity can be reproduced by selection of the correct amounts of acid and molybdate, and it was found that the required molar ratio of nitric acid to molybdate was 2–3 : 1. However, with 1.25 *N* nitric acid and 60 m*M* molybdate reproducible colours can be obtained which will tolerate quite an appreciable variation in reagent concentrations, *viz.* ± 0.5 *N* nitric acid and ± 10 m*M* molybdate. The rate of colour development was also dependent on the reagent concentrations. For any given acidity, the rate increased as the amount of added molybdate increased and maximum development rate occurred within the abovementioned reagent ranges. Full colour was developed within 5 min of adding the molybdate reagent. It was thus decided to use final reagent concentrations in the test solution of 1.25 *N* nitric acid and 60 m*M* molybdate. This can be achieved by using 25 ml of nitric acid (s.g. 1.16) and 10 ml of 10.5% w/v ammonium molybdate per 100 ml of final test solution. A tolerance of ± 5 ml of acid and ± 2 ml of molybdate can be allowed.

### *Combined vanado–molybdate reagent*

For routine work, a considerable saving in time would be achieved if the vanadate and molybdate reagents could be combined and if the total reaction could be carried out in the cold. Tests were made using separate and combined reagents, in the former case 3-min boiling being employed after the vanadate addition. When the combined reagent was used, it was added direct to the cold test solutions after the orthophosphate oxidation. In all cases no differences were observed in the rate of formation or in the colour intensity of the final complex. Calibration by both techniques yielded exactly the same relationship. No difference in results was obtained when a mixed reagent which had been stored for 2 months was used. As a result the combined reagent was formulated to contain 1.75 g of ammonium vanadate and 53 g of ammonium molybdate per l; 20 ml of this reagent is added to the cold test solution which is then diluted to 100 ml. A tolerance of ± 2 ml can be allowed on this addition.

### *Effect of iron concentration*

From previous experiments it became apparent that for cast iron analysis 0.3-g samples with suitable cell widths would cover phosphorus contents to 2%. For steel analysis, using 4-cm cells, 0.5-g samples would be required, and the effect of this increase in iron concentration was investigated. Mixtures of 0.5 g of pure iron and 3 mg of phosphorus were processed using acidities of 0.75–2.0 $N$ nitric acid in the final solution. Final concentrations of vanadate and molybdate were fixed at 3 m$M$ and 50 m$M$ respectively. The latter is less than the 60 m$M$ optimum and was chosen so that any adverse effects due to the increased iron concentration would be more apparent.

As the iron concentration increased, the effect of variation in acidity became more pronounced on both blank and test solutions. When the blank was used for compensation, acidity control was slightly more critical in the presence of the higher iron concentration, but the degree of control required is well within routine tolerances. The rate of colour development was independent of the variation in iron content, and since the presence of 0.5 g of iron had no detrimental effect on the reaction conditions, this sample weight was chosen for steel analysis.

### *Oxidation of phosphate and combined carbon*

After dissolution of irons and steels in nitric acid, most of the phosphorus is present as metaphosphate, and combined carbon is converted to a brown colloid which is probably a nitrated hydrocarbon. The colour of the latter varies with the conditions and shows pronounced absorption in the violet wave-band, hence gross errors will occur if it is not destroyed. The metaphosphate must be oxidised to reactive orthophosphate which process also serves to destroy the combined carbon colour. For nitric acid solutions, potassium permanganate is often used as oxidant, although ammonium persulphate has also been used. After oxidation, excess of permanganate can be reduced by sulphurous acid, hydrogen peroxide, or sodium nitrite; with persulphate, excess is destroyed by boiling.

The persulphate and the permanganate methods were investigated. With the former, a 15-min boiling time was used for oxidation and for destruction of excess oxidant; with the latter, 3-min boiling was used and excess was reduced with 20 vol. hydrogen peroxide. The peroxide excess was removed by a 3-min boil.

A sample of relatively high phosphorus content was used, *i.e.* British Chemical Standard (B.C.S.) No. 206/1; 1.38% P to compare the effects of both oxidants. Identical results were observed with between 0.05 and 2.0 g of permanganate, but with the persulphate, a minimum of 1 g was required for full oxidation.

Since permanganate is much more convenient to use and since a much smaller amount is required and conditions are less critical, it was decided to use this as oxidant.

To investigate oxidation of combined carbon a sample of relatively high combined carbon and low phosphorus content was used (B.C.S. No. 215: 0.94% C; 0.038% P), varying amounts of permanganate being used for oxidation. The same lower limit of 0.05 g proved to be sufficient, but the upper limit was reduced to 0.3 g; above this amount higher colour intensities were observed.

In view of these results, 0.1 g potassium permanganate "Analoids" were subsequently used, the time of boiling being fixed at 3 min, since times between 1 and 8 min gave identical results.

### *Effects of temperature*

Temperature variation has been quoted as having little effect within the range 20°-30°, although in some cases the temperature effect has been found to be serious. HILL[13] has reported that the effect becomes more serious as the iron concentration increases. BAGHURST AND NORMAN[1] have shown that with acidities between 0.8 and 1.2 *N* little variation of colour occurred with temperature change, whereas between 1.2 and 2.0 *N* the temperature effect increased rapidly. To investigate temperature effects on the final colour intensity, readings were made at various temperatures on processed solutions of pure iron, phosphate and iron plus phosphate. In all cases the amounts used corresponded to both low and high phosphorus contents. The relation between density and temperature was linear for all the solutions used. With the low iron, high phosphorus solutions, the iron had no effect on the rate of change of colour. With the higher iron content and cell width used for the low phosphorus solutions, a more pronounced effect was apparent in the presence of the iron.

By measuring blank and sample solutions at corresponding temperatures the temperature effect can be largely eliminated as shown in Fig. 2. Curves (*a*) were obtained when the blank solutions were measured at 20° and sample solutions at the variable temperature. Curves (*b*) were obtained when the blank and sample solutions were both measured at the indicated temperatures. Thus, provided that the blank and sample solutions are within ± 1°, measurements can be made within the range 15°-25° and relative errors will be within ±1% of the phosphorus content.

### *Development and stability*

Experiments showed that the full colour of the vanadomolybdiphosphoric acid was developed within 5 min of adding the vanado-molybdate reagent. This colour was then stable for at least 24 h. This applied to samples of both low and high phosphorus contents.

### *Interfering elements*

Graphitic carbon interferes owing to the additive absorption caused by the suspension of graphite in the solution. Appreciable amounts of silicon (about 4%) have been stated to interfere[11] owing to the possible formation of silicomolybdate, and serious interference from arsenic has been reported[8,14–17] owing to the formation of arsenic complexes. In previous methods[8,15–17], arsenic has been removed by volatilisation with brominated hydrochloric acid or with hydrobromic acid. Chromium(III) has been quoted as causing no interference[18], whereas with chromium(VI), serious interference has been reported[7,10,18]. Tungsten, if present, can be initially oxidised to tungstic oxide and then filtered off and under these conditions no interference has been reported[14,18]. For routine control work, particularly on low alloy and non-alloyed samples, it was decided to use the straightforward method without solvent extraction. To investigate the effects of interfering elements, solutions of these were added to samples of B.C.S. carbon steel, and the resulting mixtures were processed. The results may be summarised as follows:

*Graphitic carbon.* When this was separated by filtration before the absorptiometric measurement, sorption of the vanadomolybdiphosphate occurred on the filter paper leading to low results. By filtering the initial acid solution of a sample through prewetted Whatman No. 4 filter paper and washing with hot water, accurate results were obtained.

*Arsenic.* Up to 1% arsenic showed no interference and thus the volatilisation procedure for its removal need not be applied.

*Chromium.* In this method chromium is present in the final solution in the trivalent state, and this showed serious positive interference above about 1% chromium (Fig. 3).

*Zirconium.* As seen in Fig. 3, this element seriously suppressed the reaction, but up to 0.05% can be tolerated.

*Tungsten.* This can be separated as tungstic oxide by acid oxidation followed by filtration. However, even when precautions were taken to avoid coprecipitation of phosphorus and incomplete separation of tungsten, serious interference was encountered. Thus, tungsten-bearing samples cannot be analysed by this method.

*Copper, cobalt, nickel.* These elements showed positive interference which is due to the additive absorptions of the ions of these elements.

*Other elements.* The remaining elements which showed no interference are: Mn (up to 10%); Al, Pb, Mo, Si (up to 5%); Mg (up to 2%); Ti (up to 1%); Ce, V (up to 0.5%). Amounts greater than these were not investigated since these limits were sufficient for the requirements of the method.

TABLE I

RESULTS OBTAINED ON STANDARDS

| *B.S.C. No.* | *Type* | *% P* | | *% P found* | |
|---|---|---|---|---|---|
| 239/1 | Steel | 0.024 | 0.024 | 0.025 | 0.025 |
| 215 | Steel | 0.038 | 0.037 | 0.039 | 0.039 |
| 218 | Steel | 0.045 | 0.044 | 0.045 | 0.045 |
| 161/1 | Steel | 0.044 | 0.044 | 0.044 | 0.045 |
| 232 | Steel | 0.076 | 0.078 | 0.072 | 0.075 |
| 170 | Hematite Iron | 0.026 | 0.027 | 0.028 | 0.028 |
| 236/1 | Hematite Iron | 0.066 | 0.067 | 0.067 | 0.067 |
| 234/3 | Cast Iron | 0.33 | 0.32 | 0.34 | 0.34 |
| 171 | Cast Iron | 1.07 | 1.04 | 1.06 | 1.06 |
| 206/1 | Cast Iron | 1.38 | 1.36 | 1.38 | 1.36 |

### *Calibration*

Calibration was carried out by addition of known amounts of standard sodium phosphate solution to pure iron. These mixtures were processed by the full procedure, and difference drum readings were plotted against the percentage of phosphorus. Typical calibration curves are shown in Fig. 4. It is seen that a slight deviation occurred from linearity, but the curves obtained were highly reproducible.

### *Accuracy*

To test the accuracy of the method, replicate determinations were made, in random batches, on B.C.S. steels and cast irons, the results being shown in Table I. Subsequent checks on a variety of standards over several years of routine use have shown very good agreement with certified values.

## RECOMMENDED PROCEDURE

As a result of the above investigations the following procedure is recommended.

### *Reagents*

(*a*) Nitric acid. To 900 ml of water add 400 ml of concentrated nitric acid. Cool to about 20° and adjust this mixture to s.g. 1.160 (by hydrometer) by further addition of acid or water.

(*b*) Potassium permanganate. Analoids No, 4 C (0.1 g $KMnO_4$) can be conveniently used.

(*c*) Hydrogen peroxide. 20 vol. solution.

(*d*) Vanado-molybdate. Dissolve 1.75 g of ammonium vanadate in about 800 ml of hot water. Add 53 g of ammonium molybdate and stir this hot mixture until dissolved. Filter and dilute with water to 1 l.

### *Absorptiometer*

With the Spekker Absorptiometer, the following settings etc. are used, Lamp: Tungsten. Filters: Violet, Ilford No. 601. Setting: Water to water 1.00. Cells: 0.5 cm for up to 2% P (with 0.3 g sample), 4 cm for up to 0.15% P (with 0.5-g sample). Intermediate ranges can be covered by using other cell widths if desired.

### *Procedure*

A blank determination with the appropriate weight of pure iron should be carried out, using the full procedure, each day of use.

Transfer 0.5 g of sample (P to 0.15%) or 0.3 g of sample (P to 2%) to a 200-ml conical beaker. Add 25 ml of the nitric acid, cover with a clock-glass and boil gently until the sample is dissolved, taking care to avoid excessive evaporation. Add about 30 ml of water and raise to the boil. At this stage filter off graphitic carbon, if present, through a pre-wetted Whatman No. 4 filter paper and wash with hot water. To the solution add 0.1 g of potassium permanganate (1 Analoid No. 4C) and boil for 2–3 min. Add hydrogen peroxide dropwise to the boiling solution until all excess of permanganate is reduced, then boil for 2–3 min to destroy excess peroxide. Cool, add 20 ml of vanado-molybdate, mix and transfer with water washes to a 100-ml graduated flask, diluting with water. Transfer the solution to the appropriate cell and measure the colour reading on the absorptiometer. Subtract this from the blank and convert the resultant "difference" reading to % phosphorus by reference to the calibration chart.

### *Calibration*

For the above ranges the following phosphate solutions may be used:

(*a*) Low range (0–0.15% P, 0.5-g sample, 4-cm cell). 0.4583 g of anhydrous disodium hydrogen phosphate per 1 l. 1 ml = 0.02% P on a 0.5-g sample. Transfer 0, 2, 4, 6, 8 ml to beakers containing 0.5 g of pure iron and treat as described in the above procedure.

(*b*) High range (0–2% P, 0.3-g sample, 0.5-cm cell). 2.7498 g of anhydrous disodium hydrogen phosphate per 1 l. 1 ml = 0.2% P on a 0.3-g sample. Transfer 0, 2, 4, 6, 8, 10 ml to beakers containing 0.3 g of pure iron and treat as described in the above procedure. Plot "difference" readings against % P to obtain the calibration curves.

## ACKNOWLEDGEMENT

The author is indebted to The English Electric Co., Ltd. for permission to publish this paper.

## SUMMARY

A critical investigation has been made of the vanadomolybdiphosphate method for the absorptiometric determination of phosphorus in irons and steels. The reaction conditions have been standardised to produce a simple, rapid and reliable control method. The effects of interfering elements have also been studied.

## RÉSUMÉ

Une étude critique a été effectuée sur le dosage absorptiométrique du phosphore, sous forme de vanadomolybdiphosphate, dans les fers et les aciers.

## ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die absorptiometrische Bestimmung von Phosphor als Vanadomolybdiphosphat in Eisen und Stahl.

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# OXIMIDOBENZOTETRONIC ACID

## A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

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(Received January 10th, 1961)

WENGER AND DUCKERT[1] have made a critical study of various organic reagents recommended for the colorimetric determination of iron. In the past few years, a large number of compounds have been suggested for the colorimetric and spectrophotometric determination of iron. Some of these are: 4-hydroxybiphenyl-3-carboxylic acid[2], ethyl α-isonitrosoacetoacetate[3], nitroso R-salt[4], 5,6-benzoquinaldinic acid[5], α-picolinic acid and quinaldic acid[6,7], *m*-methoxy-*o*-nitrosophenol[8], iodoxine[9], 4,7-dihydroxy-1,10-phenanthroline[10], 2-fluorobenzoic acid[11], 2-acetyl-pyridine oxime[12], 4,7-diphenyl-1,10-phenanthroline[13], 3-hydroxy-2-naphthoic acid[14], quinolinic acid[15], picolinedioxime[16] and *o*-dianisidine[17]. But all these reagents suffer from the disadvantage that a strict pH control is necessary, and in many cases organic solvents are needed either to keep the complex in solution or to extract the coloured complex; also in many cases foreign ions interfere in the colorimetric determination. SANDELL[18] has described and recommended various reagents for the colorimetric determination of iron. *o*-Phenanthroline[18] is good, but has certain disadvantages: silver and bismuth give precipitates with the reagent, and the method cannot give accurate results when large amounts of metal ions like zinc, tungstate, nickel, cobalt and tin are present with iron. Although the thiocyanate method[19] is extensively used, the method suffers from the following drawbacks: a large excess of the reagent is necessary for complete colour development, the method can be used only within a narrow pH range, fluoride, phosphate, oxalate, vanadate, molybdenum and tungsten interfere and the colour fades rapidly with time.

During the course of our studies of certain derivatives of benzotetronic acid as analytical reagents[20-22], it has been observed that oximidobenzotetronic acid (or α-isonitrosobenzotetronic acid) can be successfully employed for the spectrophotometric determination of iron(II). ANSCHÜTZ[23] first prepared this compound and after analysis of its silver salt gave $C_9H_4O_4NAg$ as the molecular formula for the salt. This author also reported the formation of a blue colour when an aqueous suspension or alcoholic solution of the reagent was treated with an aqueous solution of iron chloride. We have now observed that when a freshly prepared alcoholic solution of this reagent is treated with an aqueous solution of iron(II), a deep blue water-soluble complex is instantaneously produced. Although a similar reaction is seen with iron(III), we have studied only the former reaction, as it is more sensitive and the colour development is instantaneous. The iron(II)-complex is quite stable and the intensity of the colour remains unchanged between the wide pH range of 2.5 and 10.0. The complex obeys Lambert-Beer's law between the concentration range of 0.54–5.4 p.p.m. of iron and the optical density is unaffected within the temperature range of 10–50°. The reagent is quite selective for iron; only cobalt, nickel, cerium(IV) and zirconium give coloured complexes but they interfere only when present in quantities more than fifty times that of iron.

## EXPERIMENTAL

### *Preparation of oximidobenzotetronic acid*

4-Hydroxycoumarin, an easily available substance was prepared by the method of STAHMAN *et al.*[24], and was readily converted into oximidobenzotetronic acid by the action of nitrous acid as described by ANSCHÜTZ[23]. The strength of the solution of oximidobenzotetronic acid in alcohol employed was $1.0 \cdot 10^{-3}$ *M*.

### *Reagents*

Ferrous ammonium sulphate (*pro analysi*) was used. Hydroxylamine hydrochloride was used as the reducing agent to ensure that all iron was in the divalent state. All other reagents were of B.D.H. (A.R.) or Merck *pro analysi* quality.

### *Apparatus and instruments*

A Hilger U.V. Spectrophotometer was employed for the absorption spectrum of oximidobenzotetronic acid. All other spectrophotometric measurements in the wavelength range of 370 mμ–750 mμ were made with the Unicam Spectrophotometer Model SP 600; 1-cm absorption cells were used.

All pH measurements were made with the help of a Beckmann pH Meter Model H 2.

### *Absorption spectra*

The absorption spectrum of oximidobenzotetronic acid was ascertained in the utraviolet as well as in the visible region. Maximum absorption was observed at

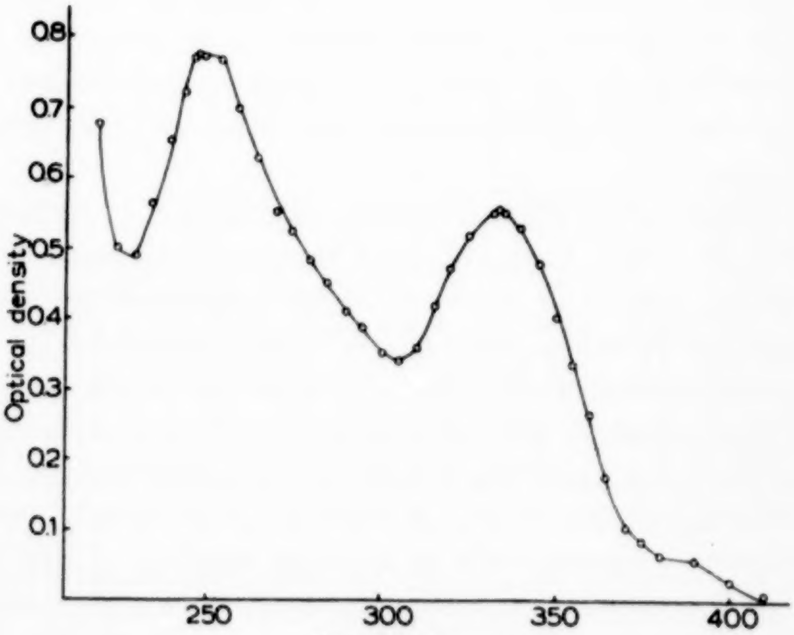

Fig. 1. U.V. spectrum of oximidobenzotetronic acid.

249 mμ and 334 mμ, the former being more pronounced than the latter (Fig. 1), and no absorption maximum was observed in the visible region. The absorption spectra of the iron(II)-oximidobenzotetronic acid complex was determined at various pH values between 2.0 and 10.0, pH adjustments being made with dilute solutions of hydrochloric acid and sodium hydroxide. The complex exhibited maximum absorption at 625 mμ in every case (Fig. 2), which indicated that only one type of complex was produced under these conditions of pH. The complex after partial extraction with chloroform exhibited the same absorption maximum. A 50% (v/v) ethanolic solution of the complex also had the absorption maximum at 625 mμ; the absorption due to the reagent at this wavelength was found to be negligible. The wavelength 625 mμ was, therefore, chosen in the subsequent investigations.

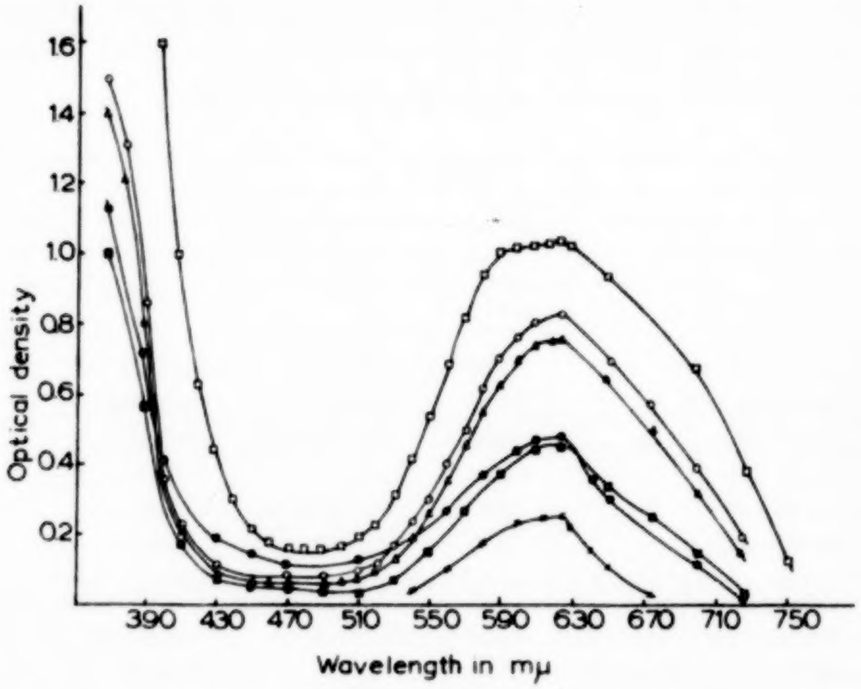

Fig. 2. Absorption spectrum of iron(II)-oximidobenzotetronic acid complex. $\lambda_{max} = 625$ mμ ● at pH 10.0; ■ at pH 8.0 and 6.0; ○ at pH 4.0; △ at pH 2.0; □ in chloroform; × in 50% (v/v) ethanol.

### *Minimum amount of oximidobenzotetronic acid necessary for the determination of iron (II)*

The optical densities at 625 mμ of a series of solutions containing oximidobenzotetronic acid and iron(II) in the molar ratio of 0.5 : 1 to 9 : 1 were determined. A plot of the results showed that maximum density was reached at the molar ratio of 4 and remained constant thereafter. For the determination of iron, however, the molar ratio of the reagent to iron was maintained at 10 in the subsequent studies.

### *Effect of pH on the optical density of iron(II)-oximidobenzotetronic acid complex*

The stock solution of the complex was $6.6 \cdot 10^{-5}$ *M* with respect to iron; 10 ml of this solution was taken in a 25-ml measuring flask and the volume made up to the mark using dilute solutions of hydrochloric acid and sodium hydroxide to bring the resultant solution to a pH value within the range of 2.5–10. It was found that the absorption by the complex is at a maximum and remains unchanged over this wide pH range. The pH of each of the solutions was determined using a suitable glass electrode.

### *Stability of the colour of the complex*

The colour of the complex was found to be stable and no change in the optical density could be observed even after keeping the complex for 36 h. The effect of temperature on the optical density of the complex was also studied using a thermostat for temperatures above 25° and a refrigerator for lower temperatures. No change in the optical density of the complex was observed between 10° and 50°. The colour of the complex is, however, destroyed on continuous heating at 100°.

The complex was found to obey Lambert-Beer's law in the concentration range of 0.54–5.4 p.p.m. of iron and in the pH range of 2.5 and 10.0.

TABLE I

INTERFERENCES

| *Ion* | *Taken as* | *p.p.m. tolerated* |
|---|---|---|
| Acetate | Ammonium salt | 600 |
| Bromide | Potassium salt | 1500 |
| Borate | Sodium salt | 600 |
| Chloride | Sodium salt | 2000 |
| Citrate | Sodium salt | 800 |
| Fluoride | Sodium salt | 400 |
| Iodide | Potassium salt | 800 |
| Oxalate | Potassium tetroxalate | 400 |
| Phosphate | Sodium hydrogen salt | 720 |
| Salicylate | Sodium salt | 500 |
| Tartrate | Sodium salt | 600 |
| Thiocyanate | Potassium salt | 1500 |
| Aluminium | Sulphate | 200 |
| Beryllium | Nitrate | 400 |
| Cadmium | Chloride | 1020 |
| Cerium(III) | Nitrate | 400 |
| Cerium(IV) | Ammonium nitrate | 100 |
| Chromium | Sulphate | 160 |
| Cobalt | Sulphate | 400 |
| Copper | Sulphate | 720 |
| Lanthanum | Nitrate | 13200 |
| Lead | Nitrate | 200 |
| Manganese | Sulphate | 400 |
| Mercury(II) | Chloride | 1200 |
| Molybdenum | Ammonium molybdate | 920 |
| Nickel | Sulphate | 200 |
| Silver | Nitrate | 1440 |
| Thorium | Nitrate | 400 |
| Titanium | Pot. titanyl oxalate | 200 |
| Wolfram | Sodium tungstate | 1200 |
| Uranium(VI) | Uranyl nitrate | 300 |
| Yttrium | Nitrate | 3600 |
| Zirconium | Oxychloride | 120 |
| Zinc | Sulphate | 1110 |

### *Interference due to foreign ions*

The stock solution of the complex was $1 \cdot 10^{-4}$ *M* with respect to iron, and the mole ratio of the reagent to iron was 10. 10 ml of this solution was transferred to a 25-ml standard flask and mixed with a known amount of a solution of a foreign salt, and the volume was made up to 25 ml with water. The optical density was determined within 10 min of mixing. The concentration of the foreign salt in the complex solution was progressively increased till the optical density changed by 2% from the theoretical values. The concentrations of the ions tested which caused no interference are given in Table I.

No interference was caused by tin(II) or sulphite. Hydroquinone was used as the reducing agent when the interference of silver was studied.

### *Recommended procedure*

The given iron(II) solution at pH 2.5–10.0 containing 0.54–5.4 p.p.m. of iron is treated with a fresh solution containing a ten-fold amount of the reagent in the minimum amount of alcohol within the temperature range 10–50°. The optical density at 625 mμ of the ferrous complex so produced is measured and the concentration of iron deduced from a standard calibration curve obtained under similar conditions.

## ACKNOWLEDGEMENTS

The authors are grateful to Prof. T. R. SESHADRI, F.R.S., Head of the Chemistry Department, for his kind interest and helpful discussions, and to the Department of Atomic Energy, Govt. of India, for financial assistance.

## SUMMARY

Oximidobenzotetronic acid is proposed for the spectrophotometric estimation of iron. A freshly prepared alcoholic solution of the reagent produces a deep blue water-soluble complex with an aqueous solution of iron(II). The complex is stable and its optical density is constant at pH 2.5–10. Lambert-Beer's law is followed from 0.54–5.4 p.p.m. of iron at 625 mμ; temperature has no effect between 10° and 50°. The reagent is highly selective for iron.

## RÉSUMÉ

Un nouveau réactif, l'acide oximidobenzotétronique, est proposé pour le dosage spectrophotométrique du fer(II). Ce réactif est très sélectif et donne un complexe bleu très stable.

## ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Fe-(II) wird Oximidobenzotetronsäure als Reagenz vorgeschlagen, das mit Fe-(II) einen stabilen, blau gefärbten Komplex bildet.

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# SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF METALS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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(Received January 13th, 1961)

## INTRODUCTION

Although dithizone and oxine have been widely accepted as important chromogenic agents for metals, many other heavy metal ions interfere in determinations with these reagents. The aim of this investigation was to develop rapid direct and sensitive methods with 1-(2-pyridylazo)-2-naphthol[1-3] in which possible interferences would be minimized or eliminated.

The determination of cadmium at the low concentration which may be of nuclear chemical significance requires a highly sensitive and selective method. The dithizone method[4] has the requisite sensitivity; however, nearly a score of other metals react with dithizone to produce intense colours, most of which resemble that of cadmium. The growing importance of yttrium in the fields of metallurgy and nuclear chemistry has necessitated the development of a method for the rapid determination of yttrium. A sensitive colorimetric method for the determination of yttrium with arsenazo[5] has been described. But, in this method many heavy metals, alkali metals and rare earth interfere. Recently, a pyrocatecholviolet method[6] has been reported, but, as in the case of arsenazo, it is not particularly selective. Although several colorimetric methods have been described for the determination of manganese (especially the permanganate method) and mercury, the colour reactions are not very sensitive or selective. In the establishment of methods for the separation and the spectrophotometric determination of metals by solvent extraction as 1-(2-pyridylazo)-2-naphtholates, procedures have already been proposed for uranium[7-9], indium[10], and for the simultaneous determination of indium and iron[10]. In a previous paper[3], the author has indicated that cadmium, manganese, mercury, gallium, iron, and yttrium react with 1-(2-pyridylazo)-2-naphthol(PAN) to form stable chelates. Recently, HNILIČKOVÁ AND SOMMER[11] reported that the sensitivity of reaction with metals of PAN analogues decreased as follows. PAN > PAR (4-(2-pyridylazo)-resorcinol) > Pyridine-2-azo-1-dihydroxynaphthalene-2,3-sulfonic acid-6 > PAO (4-(2-pyridylazo)-orcinol) > Pyridine-2-azo-2-chromotropic acid > Pyridine-2-azo-2-amino-1-hydroxy-8-naphthalene-3,6-disulfonic acid, hence the present study was confined to PAN. The reaction with PAN is extremely sensitive and quite selective so that many commonly associated ions do not interfere and the reaction can be applied to the solvent extraction and spectrophotometric determination of these metals.

From dilute acid or alkaline solutions of the above metals a red or dull red precipitate is obtained when a methanolic solution of PAN is added; this precipitate is readily extracted by a suitable organic solvent to give red or dull red colour. PAN chelates are sensitive to changes in hydrogen ion and the reagent is therefore comparatively selective in its action. In the present paper, the detailed conditions for the spectrophotometric determinations of these metals by solvent extraction are described. The various recommendations are summarized in Table I.

The method has been applied to (*1*) determination of iron in clay and anorthosite, (*2*) separation of manganese from nickel, and (*3*) separation of yttrium from lanthanum and cerium.

TABLE I

DATA ON THE ANALYTICAL WORK

| *Metal* | *Colour of chelate* | *pH conditions* | *solvent* | *Wave length (mμ)* | *Range of detn. (p.p.m.)* |
|---|---|---|---|---|---|
| $Mn^{+2}$ | wine red | 9 ∼10 | ether | 560 | 0 ∼1 |
| $Cd^{+2}$ | red | 8.7 ∼10 | chloroform | 555 | ∼2.5 |
| $Hg^{+2}$ | red | 6 ∼ 7.5 | chloroform | 560 | ∼2 |
| $Ga^{+3}$ | red | 3.6 ∼ 5 | chloroform | 560 | ∼3 |
| | | | aqueous soln. | 515, 530 | ∼5 |
| $Fe^{+3}$ | dull red | 4 ∼ 8 | benzene | 775 | ∼4 |
| $Y^{+3}$ | red | 8.5 ∼11 | ether[a] | 560 | ∼1 |

[a] In a previous article[3], Table I on p. 368, column 5, line 15, yellow should read red.

## EXPERIMENTAL

### *Apparatus*

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, with 1-cm cells. A Horiba M-3 type pH meter was used.

### *Standard solution of metals*

*Cadmium*: This solution was prepared by dissolving 0.5903 g of pure metal (99.9%) in nitric acid and diluting to 500 ml with redistilled water.

*Gallium*: This solution was prepared by dissolving 0.500 g of pure metal (Yokozawa Chem. Co., 99.99%) in hydrochloric acid and diluting to 500 ml with redistilled water.

*Manganese*: This solution was prepared by dissolving pure manganese sulfate in redistilled water.

*Mercury*: A solution was prepared containing 1.00 mg of mercury per ml by dissolving pure mercuric nitrate in redistilled water.

*Iron*: This solution was prepared by dissolving 0.517 g of electrolytic iron in 10 ml of concentrated nitric acid and diluting to 500 ml with redistilled water.

*Yttrium*: A solution was prepared by dissolving 0.200 g of pure yttrium nitrate hexahydrate (British Drug Houses Ltd.) in 200 ml of slightly acidic solution.

Gallium, cadmium and yttrium solutions were standardized gravimetrically as oxinate, and the manganese solution was standardized gravimetrically as $Mn_3O_4$.

### *Other reagents*

1-(2-Pyridylazo)-2-naphthol(PAN) solution: A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in pure methanol, filtering through glass wool, and diluting to 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution: Sodium acetate–acetic acid and ammonium chloride–ammonia mixed solutions were used for the pH adjustment.

0.2 *N* KCN, 0.2 *N* NaF, 10% sodium citrate, and 0.1 *N* EDTA (disodium salt) solutions were used. Organic solvents were purified by the normal methods.

All other reagents used in this work were made from analytical grade chemicals or from purified materials and all solutions were prepared with redistilled water.

### *General procedure*

Transfer an aliquot of the slightly acid solution containing appropriate amounts of the required metals to a separatory funnel, and dilute to approximately 20 ml. Add 1 ml of 0.1% PAN solution and 5 ml of the buffer solution and allow to stand for several minutes. Then add exactly 10.0 ml of organic solvent to the mixture and shake vigorously for 1–2 min. Centrifuge the extract or aqueous phase and measure the absorbance at a definite wavelength against a reagent blank or water (see Table I for the correct conditions for each metal).

### *Solvent for extraction*

The complex of manganese was most efficiently extracted with ether or chloroform, the iron complex with benzene or chloroform, the yttrium complex with ether, the gallium complex with chloroform, the cadmium complex with chloroform, ether, benzene or carbon tetrachloride, and the mercury complex with chloroform or benzene.

### *Absorption spectra*

The absorption spectra of the chelates formed with cadmium, manganese, gallium, yttrium, iron, and mercury are shown in Figs. 1–6 respectively. The maximum absorption of the yttrium chelate in ether appears at 530 and 560 mμ. The absorption maxima of the manganese chelate in ether and of gallium and cadmium in chloroform

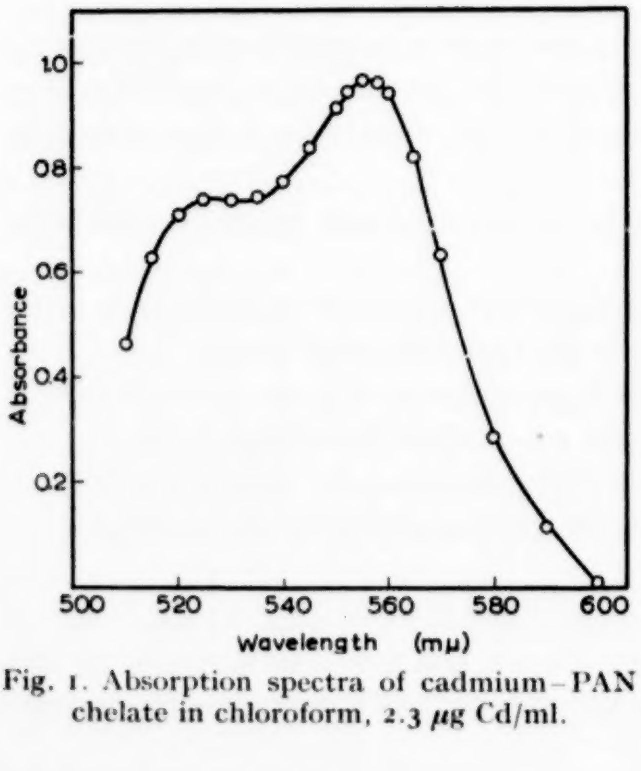


Fig. 1. Absorption spectra of cadmium–PAN chelate in chloroform, 2.3 μg Cd/ml.

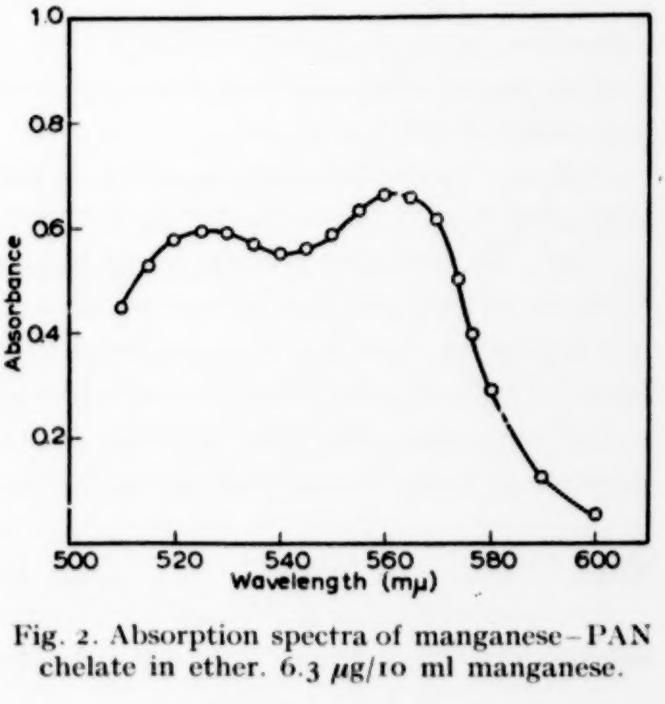


Fig. 2. Absorption spectra of manganese–PAN chelate in ether. 6.3 μg/10 ml manganese.

appear at 560, 555, and 560 mμ respectively. In benzene solution the iron chelate has an absorption maximum at 775 mμ. Although gallium chelate cannot be extracted by ether, the excess of reagent can be easily extracted into the organic layer, the gallium chelate remaining in the aqueous layer as a true solution. In this aqueous solution the gallium chelate has absorbance maxima at 515 and 530 mμ.

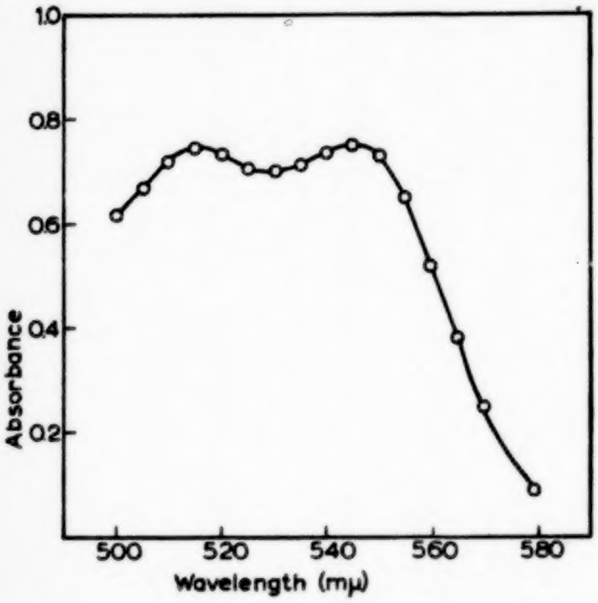


Fig. 3. Absorption spectra of gallium-PAN chelate in aqueous solution, against water.

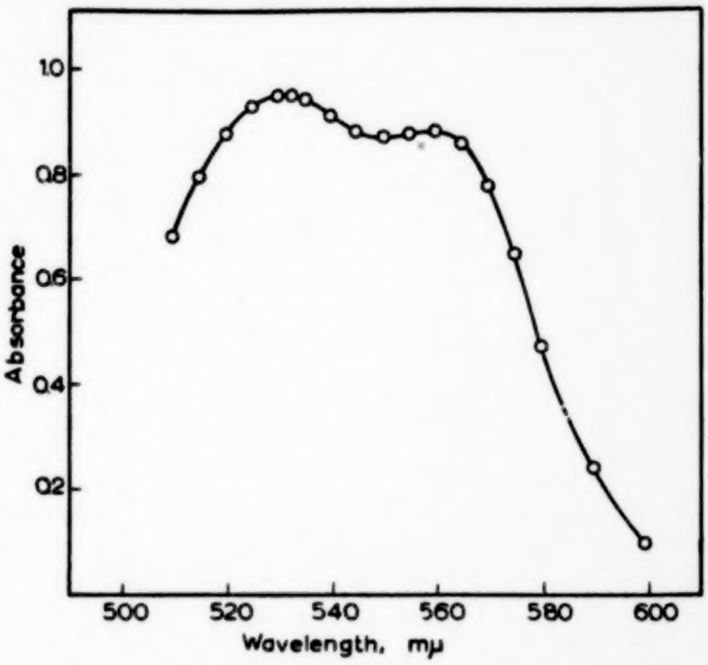


Fig. 4. Absorption spectra of yttrium-PAN chelate in ether extract.

*Effect of pH*

A series of solutions containing definite amounts of the required metal and 1 ml of 0.1% PAN solution was prepared. Sodium acetate-acetic acid and ammonium chloride-ammonia were used for the pH adjustment.

The results obtained show that the optimum pH range of manganese, cadmium,

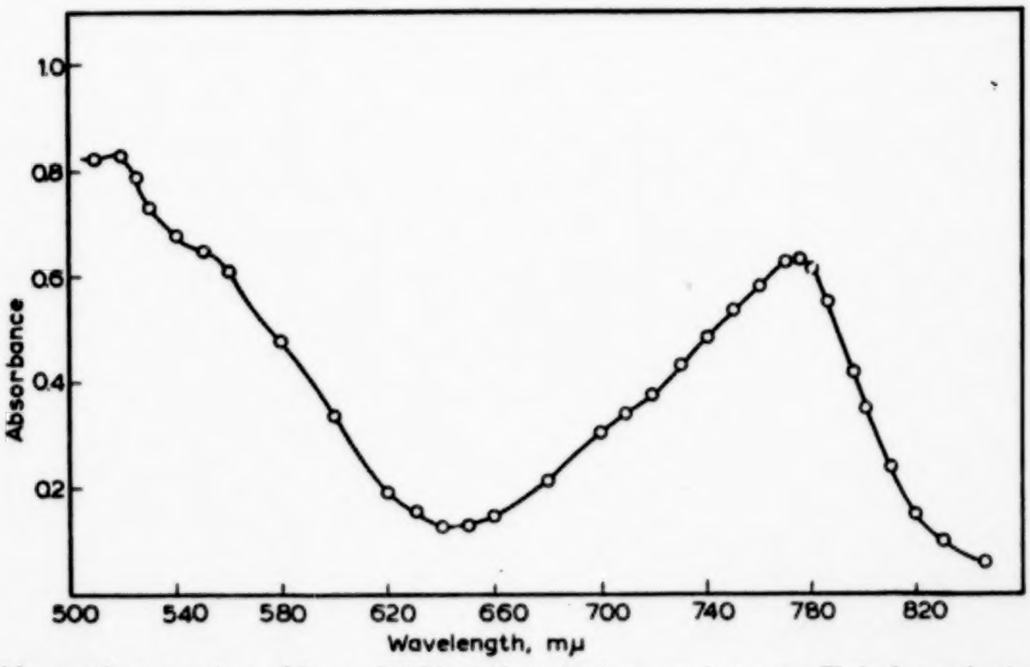


Fig. 5. Absorption spectra of iron-PAN chelate in benzene. 2.1 μg Fe/ml, against reagent.

mercury, gallium, iron, and yttrium were from 5 to 9, from 8.7 to 10, from 6 to 7.5, from 3.6 to 5, from 4 to 8, and from 8.5 to 11 respectively. At higher pH (above 7) no significant complex between gallium and PAN was formed. Above pH 11, the complexes of manganese and cadmium could not be extracted completely by chloroform, and below pH 7, no significant complexes of manganese, yttrium and cadmium were formed. Also, below pH 3 and above pH 10, the iron chelate could not be extracted completely with benzene.

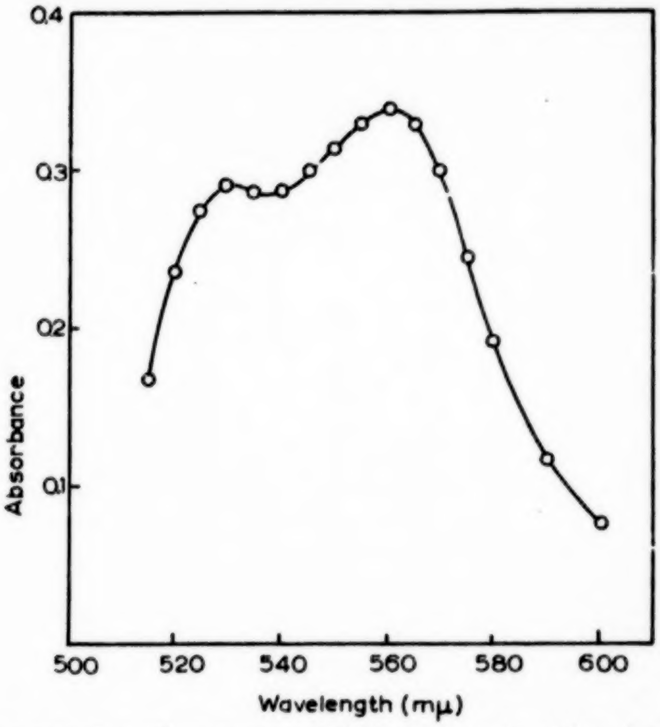


Fig. 6. Absorption spectra of mercury–PAN chelate in chloroform. 1.6 μg/ml Hg.

### *Beer's law*

The absorbances of the metal chelates in organic solvents or aqueous solution were found to be linearly related to the concentration of metals. The results show that the manganese, cadmium, mercury, gallium, iron, and yttrium complexes followed Beer's law, at least in the range up to 10 μg, 50 μg, 20 μg, 30 μg, 50 μg, and 10 μg resp.

### *Effect of reagent concentration*

The PAN concentration was varied from 0.2 to 1 ml, keeping other variables constant (Table II). 1 ml of 0.1% PAN solution suffices to complex 10 μg of manganese, 25 μg of cadmium, 15 μg of mercury, 30 μg of gallium, 40 μg of iron and 10 μg of yttrium. With higher concentrations the absorbance is essentially constant.

TABLE II

EFFECT OF CONCENTRATION OF PAN

| *0.1% PAN soln. added ml* | *Mn abs. at 560 mμ* | *Cd abs. at 555 mμ* | *Fe abs. at 775 mμ* | *Ga abs. at 560 mμ* | *Y abs. at 560 mμ* |
|---|---|---|---|---|---|
| 0.2 | 0.592 | 0.400 | 0.350 | 0.473 | 0.821 |
| 0.4 | 0.620 | 0.730 | 0.610 | 0.805 | 0.820 |
| 0.6 | 0.690 | 0.940 | 0.628 | 1.130 | 0.820 |
| 0.8 | 0.680 | 0.950 | 0.628 | 1.142 | 0.822 |
| 1.0 | 0.690 | 0.950 | 0.628 | 1.140 | 0.822 |

### *Time of standing and colour stability*

The time required for the complete colour development of PAN with manganese, cadmium, mercury, gallium, iron, and yttrium were 5, 5, 10, 30, 5, and 2 min resp. (Table III).

TABLE III

TIME OF STANDING

| *Time* *min* | *Mn abs. at 560 mμ* | *Cd abs. at 555 mμ* | *Fe abs. at 775 mμ* | *Ga abs. at 560 mμ* | *Y abs. at 560 mμ* |
|---|---|---|---|---|---|
| 2 | 0.700 | 1.04 | — | 0.615 | 0.780 |
| 5 | 0.695 | 1.06 | 0.940 | 0.795 | 0.780 |
| 10 | — | 1.07 | 0.940 | 0.785 | 0.785 |
| 15 | 0.695 | 1.07 | — | 1.087 | 0.800 |
| 30 | 0.696 | 1.08 | 0.942 | 1.140 | 0.775 |
| 60 | 0.698 | 1.07 | 0.950 | 1.140 | 0.780 |

TABLE IV

COLOUR STABILITY OF YTTRIUM CHELATE IN ETHER

| *Time* *min* | *Absorbance at 560 mμ* |
|---|---|
| 5 | 0.820 |
| 10 | 0.818 |
| 15 | 0.785 |
| 30 | 0.758 |
| 60 | 0.724 |

After this time, the colour of the extract was very stable, except in the case of yttrium, and suitable for quantitative work. Although the colour of the ether extract of the yttrium chelate was not very stable when compared with those of other metals its stability was sufficient for spectrophotometric determination. The results obtained are given in Table V.

### *Composition of the coloured complex*

The empirical formula of the coloured complexes of the metals was determined by adopting the continuous variation and the mole ratio methods. The results obtained are given in Table V.

TABLE V

COMPOSITION OF THE COLOURED COMPLEX

| | | |
|---|---|---|
| $[MePy_2^*]^0$ | .... | $Mn^{+2}$, $Cd^{+2}$, $Ni^{+2}$ $(UO_2^{+2})$ |
| $[MePy_2]^+$ | .... | $Fe^{+3}$, $Y^{+3}$, $(In^{+3},Co^{+3})$[a] |
| $[MePy]^{+2}$ | .... | $Ga^{+3}$, $(Tl^{+3})$[b] |
| $[MePy]^0$ | .... | $(VO_2^+)$[c] |
| $[MePy]^+$ | .... | $(Pd^{+2},Cu^{+2})$[d] |

[a] see ref.[12]

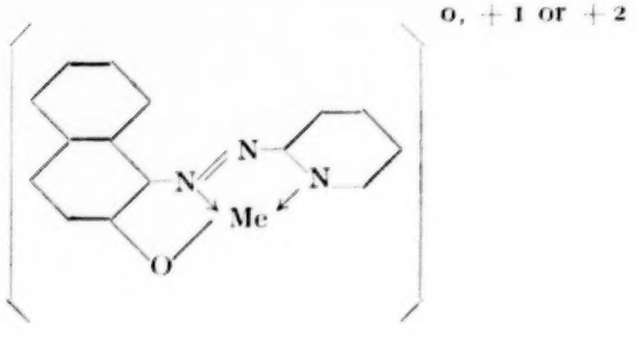
[b] see ref.[13]

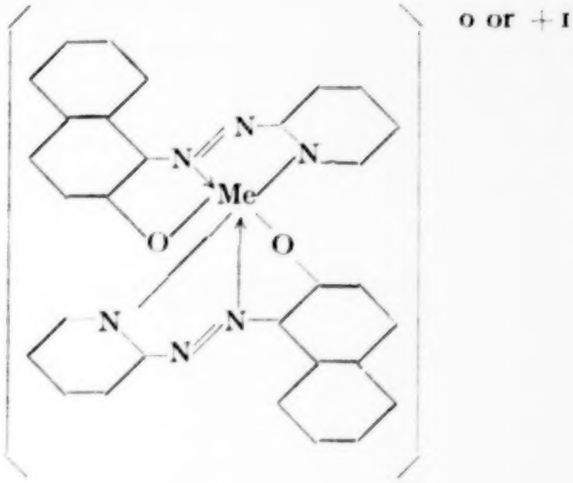
[c] see refs.[14,15]

[d] see refs.[16–19]

* Py ∼ basic form of PAN

Metals presumably form a complex similar to the structure below:





*Interfering ions*

To study the effect of various metals on this determination of these metals, a series of solutions containing the metal concerned and the other metals was treated according to the procedure. The results obtained are given in Table VI.

Chloride, bromide, sulfate, nitrate, and acetate as their sodium, potassium, or ammonium salts did not interfere. The strong interference of iron can be avoided by means of a simultaneous determination or masking with citrate. Interferences of several other metals could be removed by the use of suitable masking agents or by back-extraction.

*Back-extraction*

The selectivity of extraction and determination of metals could be increased by back-washing or back-extraction. Table VII shows the possibility of the back-extraction of some metal-PAN chelates from the organic layer.

*Effect of complexing agents*

Citrate, cyanide, fluoride, and EDTA were examined as sequestering agents for the masking of various metals.

In Table VIII, the effects of these masking agents on the chelate formation are given and, in Table IX, the effects of cyanide and citrate on the determination of manganese are given. PAN forms many insoluble chelates, but in the presence of EDTA, only uranium precipitated. Interference from cadmium, mercury, iron, nickel, zinc, cobalt, gallium, and bismuth can be obviated by masking with potassium cyanide. The complexing of metals with cyanide, followed by the selective demasking of zinc and cadmium cyanide complexes with formalin has been used for the determination of these metals with PAN in the presence of nickel[20].

## APPLICATIONS

*I. Determination of iron in clay and anorthosite.* In order to test the reliability of the proposed procedure, the determination of iron in clay and anorthosite was carried out. The method should also be useful for the determination of very small amounts of iron in a wide variety of samples.

0.500 g of sample powder was weighed into a platinum crucible, dissolved in the

TABLE VI

EFFECT OF FOREIGN IONS

| *Ion added* | *Amount added* $\mu g$ | *Added as* | *Found** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Cd* | *Mn* | *Fe* | *Ga* | *Y* | *Hg* |
| $Al^{+3}$ | 10000 | $Al(NO_3)_3$ | 20.5 | — | — | — | — | — |
| | 5000 | | 20.0 | — | 20.0 | 46.3 | — | — |
| | 2500 | | 20.0 | — | — | — | — | — |
| | 1000 | | 20.0 | 5.0 | — | — | 7.1 | — |
| | 500 | | — | — | — | — | 7.5 | 9.2 |
| $Be^{+2}$ | 400 | $BeCl_2$ | — | — | — | 46.0 | 7.5 | — |
| | 200 | | 20.0 | — | — | — | — | — |
| $Bi^{+3}$ | 500 | $Bi(NO_3)_3$ | 20.0 | 5.1 | — | — | — | — |
| | 250 | | — | — | — | 48.2 | — | 12.4 |
| | 50 | | — | — | 19.7 | — | — | — |
| $Cr^{+3}$ | 200 | $CrCl_3$ | 20.5 | 5.4 | 20.0 | — | — | — |
| | 100 | | — | — | — | — | 7.8 | — |
| $Co^{+2}$ | 5 | $CoSO_4$ | — | — | 20.0 | — | — | — |
| $Cu^{+2}$ | 100 | $CuSO_4$ | — | — | 19.4 | — | — | — |
| $Cd^{+2}$ | 100 | $Cd(NO_3)_2$ | — | — | 20.0 | 47.5 | — | 20.0 |
| $Ti^{+4}$ | 200 | $Ti(SO_4)_2$ | 19.5 | — | 19.7 | 62.6 | — | — |
| $Mn^{+2}$ | 300 | $MnSO_4$ | — | — | — | 60.0 | — | 12.5 |
| | 100 | | — | — | 19.7 | — | — | — |
| $Mo^{+6}$ | 50 | $(NH_4)_6Mo_7O_{24}$ | — | — | 20.0 | — | 7.3 | — |
| $Ni^{+2}$ | 150 | $NiSO_4$ | — | — | 19.9 | — | 7.4 | — |
| | 100 | | — | — | — | — | 7.4 | — |
| $Pb^{+2}$ | 1000 | $Pb(NO_3)_2$ | 23.5 | — | 19.2 | — | — | 10.5 |
| | 500 | | 23.2 | 5.5 | — | 48.5 | — | — |
| $Zn^{+2}$ | 100 | $ZnSO_4$ | — | — | 19.8 | — | 7.3 | — |
| $Mg^{+2}$ | 500 | $MgCl_2$ | 20.9 | 5.2 | — | 50.6 | 7.3 | 11.6 |
| $Ca^{+2}$ | 100 | $CaCl_2$ | — | — | — | — | 7.8 | — |
| $As^{+3}$ | 250 | $K_3AsO_3$ | 20.7 | 5.4 | — | 47.0 | — | — |
| $Sb^{+4}$ | 250 | $SbCl_4$ | 19.0 | 4.9 | — | 50.6 | — | — |
| $Sn^{+4}$ | 200 | $SnCl_4$ | — | — | — | — | 7.5 | — |
| $In^{+3}$ | 200 | $InCl_3$ | 19.8 | — | — | — | — | — |
| $Th^{+4}$ | 200 | $Th(NO_3)_4$ | 21.4 | 5.1 | — | — | 6.0 | — |
| $Zr^{+4}$ | 100 | $Zr(SO_4)_2$ | — | — | 19.0 | — | — | — |
| $Tl^{+}$ | 200 | $TlNO_3$ | — | — | — | 47.0 | — | 12.0 |
| $WO_4^{-2}$ | 200 | $Na_2WO_4$ | 20.0 | 5.0 | — | 41.0 | — | — |
| $VO_4^{-3}$ | 200 | $Na_3VO_4$ | 19.7 | 4.8 | — | — | 7.3 | — |
| $F^{-}$ | 200 | NaF | 20.7 | 5.2 | — | 45.0 | — | 12.0 |
| | 100 | | — | — | — | — | 6.8 | — |
| $CN^{-}$ | 5 ml 0.2 *N* | KCN | — | — | — | — | 7.5 | — |
| $PO_4^{-3}$ | 1000 | $KH_2PO_4$ | 19.3 | — | — | — | — | 10.0 |
| $SO_2^{-2}$ | 500 | $NaSO_4$ | — | — | — | — | 7.7 | — |
| $NO_3^{-}$ | 500 | $KNO_3$ | — | — | — | — | 7.0 | — |
| citrate | 10% 1 ml | — | 19.0 | — | — | — | — | 11.0 |

* Cd 20.0, Mn 5.0, Fe 20.0, Ga 47.0, Y 7.4 and Hg 12.0 $\mu g$ taken respectively.

usual way and then diluted appropriately in a volumetric flask. Iron was determined by the procedure mentioned above. The results obtained are given in Table X.

*II. Simultaneous determination of iron and other metals.* The ferric chelate of PAN in organic solvents has its absorbance maximum at 765–775 m$\mu$ approximately. On

## TABLE VII

### BACK-EXTRACTION

| *Metals* | *with 0.2 N KCN soln.* | *with pH 4.5 buffer soln.* |
|---|---|---|
| $Cd^{+2}$ | possible | possible |
| $Mn^{+2}$ | impossible | possible |
| $Zn^{+2}$ | possible | impossible |
| $Ni^{+2}$ | impossible | impossible |
| $Cu^{+2}$ | possible | impossible |
| $Hg^{+2}$ | possible | possible |
| $Co^{+3}$ | impossible | impossible |
| $Fe^{+3}$ | impossible | impossible |
| $In^{+3}$ | possible | impossible |
| $Ga^{+3}$ | possible | impossible |
| $Pb^{+2}$ | possible | possible |

## TABLE VIII

### REACTIVITY OF METALS WITH PAN IN THE PRESENCE OF MASKING AGENTS

| *Metals* | *KCN* | *Citrate* | *Fluoride* | *EDTA* |
|---|---|---|---|---|
| $Mn^{+2}$ | + | + | + | — |
| $Cd^{+2}$ | — | + | + | — |
| $Hg^{+2}$ | — | + | + | — |
| $Ni^{+2}$ | — | + | + | — |
| $Co^{+3}$ | — | + | + | — |
| $UO_2^{+2}$ | + |  | + | + |
| $Ga^{+3}$ | — | — | — | — |
| $Fe^{+3}$ | — | — | — | — |
| $Y^{+3}$ | + | + | + | — |
| $In^{+3}$ | + | + | + | — |
| $Zn^{+2}$ | — | + | + | — |
| $Bi^{+3}$ | — | — | — | — |
| $La^{+3}$ | + |  |  | — |
| $Ce^{+3}$ | + |  |  | — |

+ reaction, — no reaction; 0.2 *N* KCN, 10% sodium citrate, 0.2 *N* NaF, and 0.1 *N* EDTA solution (5 ml/25 ml) respectively.

## TABLE IX

### EFFECT OF MASKING AGENTS ON ABSORBANCE OF MANGANESE

| *0.2 N KCN soln. added (ml)* | *Absorbance at 560 mμ* | *10% citrate soln. (ml)* | *Absorbance at 560 mμ* |
|---|---|---|---|
| — | 0.510 | — | 0.510 |
| 0.5 | 0.520 | 0.25 | 0.500 |
| 1.0 | 0.499 | 0.5 | 0.500 |
| 2.0 | 0.495 | 1.0 | 0.495 |
| 3.0 | 0.374 | 2.0 | 0.490 |

## TABLE X

### DETERMINATION OF IRON IN CLAY AND ANORTHOSITE

| *Sample* | *PAN method* % | *Thiocyanate method* % |
|---|---|---|
| clay | 0.14 | 0.18 |
| anorthosite | 0.17 | 0.16 |
|  | 0.08 | 0.08 |

the other hand, most other metal chelates have no absorption at this wavelength. Therefore, some metals and iron can both be determined simultaneously by the treatment mentioned above. In a previous paper[10], the author already reported a simultaneous determination of indium and iron.

*III. Separation of manganese from nickel.* A simultaneous extraction and determination of microgram amounts of nickel and manganese was carried out. The nickel and manganese could be separated quantitatively by means of back-extraction with potassium cyanide solution or by pH control.

An aliquot of the slightly acidic mixed solution of nickel and manganese was transferred to a separatory funnel, and diluted to approximately 25 ml. 2 ml of 0.1% PAN solution and 5 ml of pH 9.5 buffer solution was added, and the mixture was allowed to stand for 5 min. Exactly 10.0 ml of chloroform was added to the mixture which was then shaken vigorously for 1-2 min and the absorbance was measured at 575 mμ against a reagent blank (Ni + Mn). When a chloroform extract of the nickel and manganese chelates was shaken with 10 ml of 0.2 *N* KCN solution, the manganese chelate was destroyed and the manganese reverted to the aqueous layer. Thus, the absorbance of the chloroform solution measured again at 575 mμ allowed the determination of nickel. The amount of manganese could then be calculated from the difference of these two absorbance values. Typical results are shown in Fig. 7.

*IV. Extraction of yttrium.* Yttrium can be extracted with organic solvents after the formation of chelates with thenoyltrifluoroacetone[21] and dibutylphosphoric acid[22].

In the method described below, the solvent extraction of yttrium-PAN chelate was performed with ether and, the separation of yttrium from lanthanum and cerium was examined.

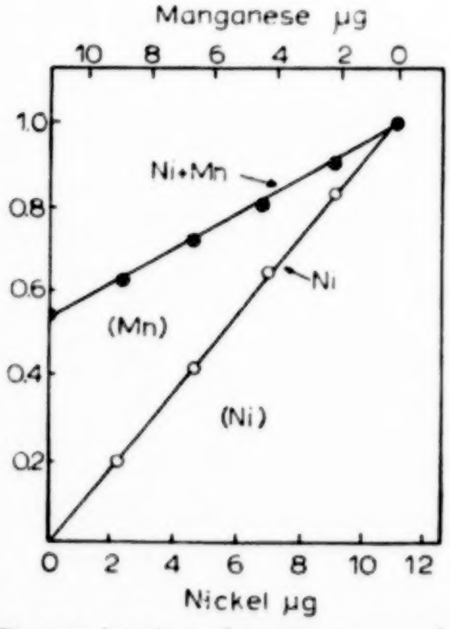


Fig. 7. Determination of manganese and nickel, $\lambda = 575$ mμ.

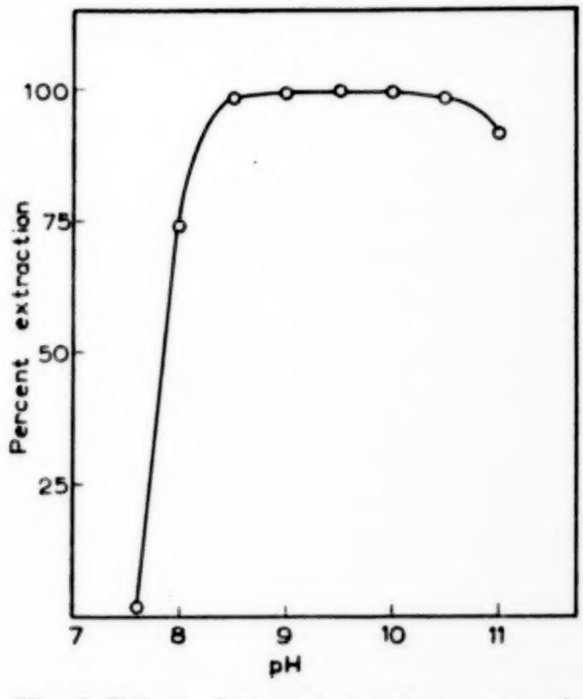


Fig. 8. Effect of pH on percentage extraction.

In order to ascertain the chemical recovery, yttrium was determined colorimetrically by the neothoron (arsenazo) method[5].

Effect of reagent concentration: 1 ml of 0.1% PAN solution sufficed for the extraction of 15 μg of yttrium. The most important fact is that yttrium chelate was found to be hardly soluble in ether, in the absence of excess reagent. Thus it was confirmed that the presence of excess reagent is a very important factor.

Effect of pH: The effect of the pH value on the extraction yield was investigated using 1 ml of 0.1% PAN solution. The experimental results are presented in Fig. 8. Almost 100% of yttrium was recovered when the extraction was made at pH values between 9 and 10.

Effect of potassium cyanide: For the separation of yttrium from many other metals, the use of potassium cyanide as a masking agent was tested. The results indicated that 2 or 5 ml of 0.2 *N* potassium cyanide solution gave no trouble as regards the extraction yield.

Procedure for the separation of yttrium: From the experimental results, the procedure for the separation of yttrium was designed as follows.

Transfer an aliquot of the sample solution, which contains up to 20 $\mu g$ of yttrium, to a separatory funnel and dilute to approximately 20 ml (if necessary, add 5 ml of 0.2 *N* potassium cyanide solution). 1 ml of 0.1% PAN solution and 5 ml of the buffer solution of pH 9–10 were added and the mixture was allowed to stand for several minutes. Exactly 10.0 ml of ether was added to the mixture which was then shaken vigorously for 1–2 min.

*Separation of yttrium from lanthanum and cerium.* In order to test the reliability of the proposed procedure, the separation of yttrium from lanthanum and cerium was carried out. The solutions containing 20 $\mu g$ of lanthanum and cerium were treated according to the above procedure. The lanthanum and cerium extracted were determined colorimetrically by the neothoron method[23,24]. The extraction yield of lanthanum and cerium was about 0.1 and 33% respectively. These results indicate that the procedure is successfully applied to the separation of yttrium from lanthanum.

## CONCLUSIONS

PAN is an extremely sensitive and comparatively selective reagent and can be used for the determination of microgram amounts of manganese, cadmium, yttrium, iron, gallium and mercury. The extraction and determination of these metals with PAN

TABLE XI

DATA ON OTHER APPLICATIONS

| *Metals* | *Colour of chelates* | *pH condition* | *Solvent* | *Wave-length mμ* | *Range of det. p.p.m.* |
|---|---|---|---|---|---|
| $Ni^{+2}$ | red | 5.5 ∼ 10 | benzene<br>chloroform | 575 | ∼1.5 |
| $Pd^{+2}$ | green | 3 ∼ 4 | chloroform | 678 | ∼16 |
| $Zn^{+2}$ | red | 6 ∼ 8[20] | chloroform | 560 | ∼1.2 |
| $UO_2^{+2}$ | red | 10 | chloroform | 560 | ∼10 |
| $V^{+5}$ | blue | 3.5 ∼ 4.5 | chloroform | 615 | ∼3 |
| | | 3 ∼ 4 | acetone | 560 | ∼6 |
| $In^{+3}$ | red | 5.3 ∼ 6.7 | chloroform | 560 | ∼5 |
| $Co^{+3}$ | green | 3 ∼ 6 | chloroform | 640 | 0.01 ∼ 2.4 |
| $Cu^{+2}$ | red | 3 ∼ 4 | 20% dioxane | 550 | — |
| | | 8 ∼ 10 | chloroform | 560 | — |

offers the definite advantage of increased selectivity by (*1*) control of pH, (*2*) selection of solvent, (*3*) using of masking agents or back-extraction. Further studies with this reagent, particularly with regard to its applications to various samples, should be quite fruitful. For reference purposes data on the analytical work done for other metals with PAN are summarized in Table XI. Bismuth, cerium, lanthanum and thorium have very sensitive colour reactions but a suitable organic solvent has not yet been found in which the stabilities of the chelates are great enough. Further work on the structure and stability of these metal chelates is now in progress.

## SUMMARY

PAN(1-(2-pyridylazo)-2-naphthol) is proposed for the solvent extraction and spectrophotometric determination of manganese, iron, cadmium, mercury, gallium, and yttrium. The reagent, which is highly specific for iron, has been applied to the determination of iron in clay and anorthosite. The separation of yttrium from lanthanum and the separation of manganese from nickel were successful.

## RÉSUMÉ

Le 1-(2-pyridylazo)-2-naphtol est proposé pour l'extraction dans solvant et le dosage spectrophotométrique du manganèse, du fer, du cadmium, du mercure, du gallium et de l'yttrium. Les séparations yttrium-lanthane et manganèse-nickel sont décrites.

## ZUSAMMENFASSUNG

Für die Extraktion durch Lösungsmittel und zur spektrophotometrischen Bestimmung von Mn, Fe, Cd, Hg, Ga und Y wird PAN (1-(2-Pyridylazo)-2-naphthol) als Reagenz vorgeschlagen. Es werden die Trennungen des Yttriums von Lanthan und des Mangans von Nickel beschrieben.

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# STUDIES ON THE EXTRACTION OF ZIRCONIUM WITH ORGANOPHOSPHORUS COMPOUNDS

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(Received January 17th, 1961)

## INTRODUCTION

Zirconium is one of the elements which are readily extracted with organophosphorus solvents, and solvent extraction with tri-*n*-butyl phosphate, TBP, has been successfully employed for the fractional isolation of zirconium from hafnium[1]. Although the solvent extraction technique is already in plant scale use for the isolation of zirconium, only a few papers have dealt with the fundamental aspects of zirconium extraction[2-5]. The present study was initiated in an attempt to obtain a pattern of zirconium behaviour during extraction with organophosphorus compounds including alkyl phosphates, phosphonate, phosphinate and phosphine oxide, so that a better selection of reagent could be made for analytical purposes.

## EXPERIMENTAL

### *Chemicals*

*Zirconium.* The radioisotope $^{95}$Zr was supplied by Oak Ridge National Laboratory in the oxalate form, which was converted to nitrate by boiling with nitric acid, and a reagent grade $ZrO(NO_3)_2$ was supplied by Yokozawa Chemical Co., Tokyo. Throughout the work $^{95}$Zr was separated from its daughter $^{95}$Nb immediately before use[5,6]. For the macroscale experiment, the zirconium solution was prepared as follows: after the tracer $^{95}$Zr was added to the solution of zirconyl nitrate, the zirconium was precipitated as the hydroxide, then dissolved in nitric acid. The above process was repeated three times in order to mix the $^{95}$Zr tracer thoroughly with the non-radioactive zirconium carrier.

*Organophosphorus solvents.* These were: Phosphates — triethyl, tri-*n*-propyl, tri-*n*-butyl, tri-iso-butyl, tri-*sec*-butyl, and tricyclohexyl phosphates; phosphonate — diethyl butyl phosphonate; phosphinate — tri-*n*-butyl phosphinate, and phosphine oxide — tri-*n*-butyl phosphine oxide. All the organophosphorus solvents were synthesized by Tama Chemical Co., Tokyo, and purified by vacuum distillation. The tri-*n*-butyl phosphine oxide was purified by recrystallization from benzene. The stock solutions of these solvents were kept in a refrigerator to avoid decomposition.

*Other chemicals.* Nitric acid and carbon tetrachloride were of reagent grade, the latter being distilled before use.

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### *Procedure*

The extraction was carried out in nitric acid media. The solvent was diluted with carbon tetrachloride. The zirconium solution and the solvent were mixed in equal volumes in a measuring flask, and shaken in a thermostat. After equilibrium had been reached, suitable volumes of both the aqueous and organic phases were taken, and the radioactivity and aqueous nitric acid concentration were determined. The solvent was pre-equilibrated with nitric acid before the extraction.

The radioactivity of $^{95}$Zr was measured with a gamma scintillation counter, and the nitric acid concentration in the aqueous phase was determined by ordinary titration.

The extraction ability of the solvent is expressed in terms of the distribution coefficient between aqueous and organic phases.

An "Infracord" spectrometer with silver chloride cells was used to measure the infrared spectra.

## RESULTS AND DISCUSSION

### *Distribution coefficient, $K_d$*

Extraction curves of typical phosphates, phosphonate, phosphinate and phosphine oxide are shown in Fig. 1. In the extraction with normal alkyl phosphates and tri-iso-butyl phosphate, the $K_d$ values increase steeply as the nitric acid concentration increases, whereas in the extraction with tri-*sec*-butyl phosphate, tricyclohexylphosphate, phosphonate, phosphinate and phosphine oxide the $K_d$ values decrease after slowly reaching a maximum at about 5–7 *M* nitric acid. The extraction ability

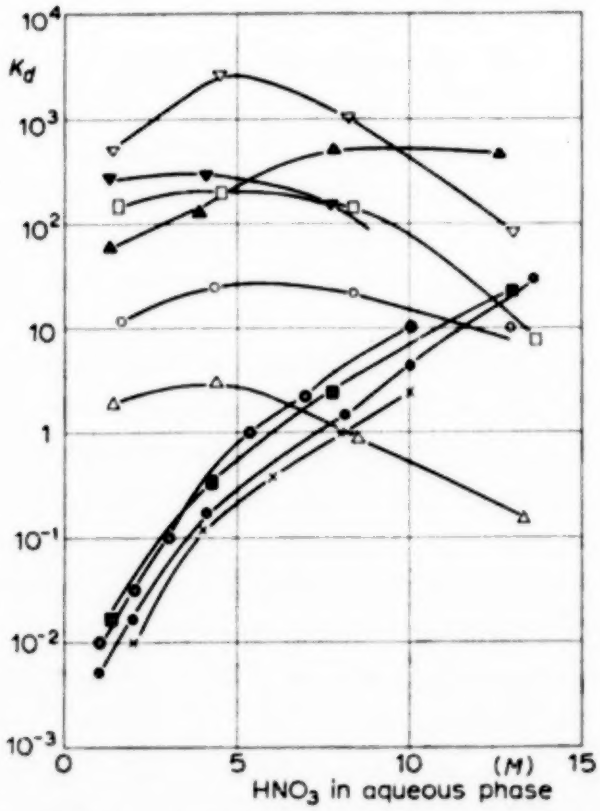

Fig. 1. Variation of $K_d$ values with aqueous nitric acid concentration. □ Tri-*n*-butyl phosphine oxide, 0.00732 *M*; ▽ Tri-*n*-butyl phosphinate, 0.00732 *M*; ○ Tri-*sec*-butyl phosphate, 0.00732 *M*; △ Diethyl butyl phosphonate, 0.00732 *M*; ▼ Tri-*sec*-butyl phosphate, 0.732 *M*; ▲ Tricyclohexyl phosphate, 0.732 *M*; ■ Tri-iso-butyl phosphate, 0.732 *M*; ● Tri-*n*-butyl phosphate, 0.732 *M*; × Triethyl phosphate, 0.732 *M*; ◎ Tripropyl phosphate, 0.92 *M*.

is affected by the substituents in the phosphoryl group as well as by the structure of the solvent. As for the phosphates with normal alkyl groups, it was observed that the extraction ability increases slightly as the carbon number of the alkyl group increases. The extraction abilities of normal alkyl phosphates are in the following order: tri-*n*-butyl phosphate > tri-*n*-propyl phosphate > triethyl phosphate.

The effect of branching in the alkyl group was examined with tri-iso-butyl phosphate, tri-*sec*-butyl phosphate and tricyclohexyl phosphate. The results indicate that branching causes a definite increase in the distribution coefficient compared to that of normal alkyl phosphates. Moreover, the existence of branching near the alkoxyl oxygen enhances the extraction ability to a remarkable extent. Tri-*sec*-butyl phosphate clearly shows a different extraction behaviour from that of tri-*n*-butyl phosphate, although tri-iso-butyl phosphate gives a curve somewhat similar to the latter. The highly branched tricyclohexyl phosphate also has a high extraction ability which is similar to that of phosphinate or phosphine oxide.

The removal of the alkoxyl oxygen definitely results in an increase in the extraction ability. But the change in the extraction ability does not follow a regular pattern, and the $K_d$ values for the phosphorus compounds tested decrease in the following order: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec*-butyl phosphate > diethyl butyl phosphonate > phosphates with normal alkyl groups.

### *Determination of the reaction mechanism and the equilibrium constant*

The extraction mechanism was examined on the normal alkyl phosphates. To determine the equation of extraction, both the solvent and acid dependences were studied. The variation of $K_d$ values with TBP concentrations, the solvent dependence, was determined over the TBP concentration range of 6–90% and nitric acid range of 2–10 *M*, and in all cases a plot of $K_d$ values *vs.* TBP concentrations gave a second power dependence. The acid dependence of the extraction is of the fourth power, and is determined by plotting the values of $K_d/[\mathrm{TBP}]^2$ against the activities of nitric acid. With other normal alkyl phosphates the same results were obtained.

To test the effect of hydrogen ion concentration, the nitric acid concentration was varied to 1, 3 and 5 *M*, while the total nitrate ion concentration was maintained at 5 *M* by addition of sodium nitrate. Zirconium was then extracted with tri-*n*-butyl phosphate. The results tabulated in Table I show no proton dependence in the extraction, hence it may be concluded that the hydrogen ion does not take part in the extraction reaction.

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION ON $K_d$ VALUES AT CONSTANT NITRATE CONCENTRATION

Total $NO_3^-$ concentration: 5 *M*, TBP concentration: 0.732 *M*

| *H conc. (M)* | 1.12 | 1.12 | 3.13 | 3.15 | 5.19 | 5.19 |
|---|---|---|---|---|---|---|
| $K_d$ | 0.35 | 0.34 | 0.37 | 0.38 | 0.49 | 0.47 |

The $K_d$ values for $10^{-5}$ *M* zirconium solution and tracer zirconium solution were found to be the same, thus there was no dependence on the zirconium concentration.

These results indicate that the reaction mechanism may be written as follows:

$$\mathrm{Zr}^{+4}_{\mathrm{aq}} + 4\,(\mathrm{NO_3^-})_{\mathrm{aq}} + 2\,(\mathrm{Org})_{\mathrm{org}} \rightarrow [\mathrm{Zr(NO_3)_4(Org)_2}]_{\mathrm{org}}$$

The evidence that two molecules of organic solvent and four molecules of nitrate ions combine with one zirconium atom suggests the charge of zirconium to be +4 over the range of 2–10 *M* nitric acid media. For the extraction of zirconium with tri-*n*-butyl phosphate, ALCOCK *et al.*[5] reported a second power solvent dependence, and MURBACH AND MCVEY[2] demonstrated that three molecules of tri-*n*-butyl phosphate combine with one atom of zirconium.

The equilibrium constant for the above extraction reaction was determined only in one case, *i.e.* with tri-*n*-butyl phosphate. This constant was calculated at various nitric acid concentrations according to the above extraction reaction, the acid concentrations being corrected by using the appropriate activity coefficients. Table II shows the values obtained, the average of which is taken as the equilibrium constant. This was determined to be $1.6 \cdot 10^{-2}$ at 23°. MURBACH AND MCVEY[2] gave a value of $5 \cdot 10^{-3}$ at 25° for the extraction of zirconium with tri-*n*-butyl phosphate, but the value was determined on the basis that three solvent molecules combined with one atom of zirconium.

TABLE II

EQUILIBRIUM CONSTANT FOR TBP EXTRACTION AT VARIOUS NITRIC ACID CONCENTRATION AT 23°

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *1. Zirconium concentration: Tracer amount* | | | | | | | |
| $HNO_3$ (*M*) | 1.0 | 1.4 | 1.8 | 2.0 | 3.0 | 4.0 | 5.2 |
| $K(\cdot 10^{-2})$ | 2.3 | 0.85 | 0.88 | 1.4 | 1.1 | 1.4 | 1.9 |
| Mean $K(\cdot 10^{-2})$ | 1.4 | | | | | | |
| *2. Zirconium concentration:* $5 \cdot 10^{-5}$ *M* | | | | | | | |
| $HNO_3$ (*M*) | 1.0 | 1.5 | 2.0 | 3.1 | 3.9 | 5.2 | 7.0 |
| $K(\cdot 10^{-2})$ | 3.8 | 1.5 | 1.3 | 1.2 | 1.1 | 1.8 | 1.3 |
| Mean $K(\cdot 10^{-2})$ | 1.7 | | | | | | |

### *Effect of temperature*

The effect of temperature was examined for the extraction with tri-*n*-butyl phosphate. The results indicate that the temperature dependence is affected by the nitric acid concentration in the aqueous phase as illustrated in Fig. 2. At low acid concentration, the $K_d$ values increase as the temperature rises, whereas an entirely opposite relationship is observed at high acid concentrations. In the intermediate range of nitric acid concentration, no appreciable temperature dependence is observed.

### *Infrared spectra*

The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with tri-*n*-butyl phosphate, diethyl butyl phosphonate, tri-*n*-butyl phosphinate and tri-*n*-butyl phosphine oxide were measured. The infrared spectrum of the extracted complex was compared to that of corresponding solvent, and changes between these two spectra were analysed.

The changes observed are not characteristic only for the zirconium complexes: the same changes are commonly observed in infrared spectra of other metal organophosphorus complexes. Although the analysis and the interpretation of the changes observed in the infrared spectra of metal organophosphorus complexes will be published as a separate paper, the following major changes are referred to here: (*1*) the shift in the P=O stretching frequency by complexing with zirconium, (*2*) the split of the ionic nitrate degenerate stretching vibration, which is attributed to the covalent nature of the complexes, and (*3*) the change in P—O—C stretching bond, the nature of which is not clearly understood as yet. Some of the typical spectra are shown in Fig. 3.

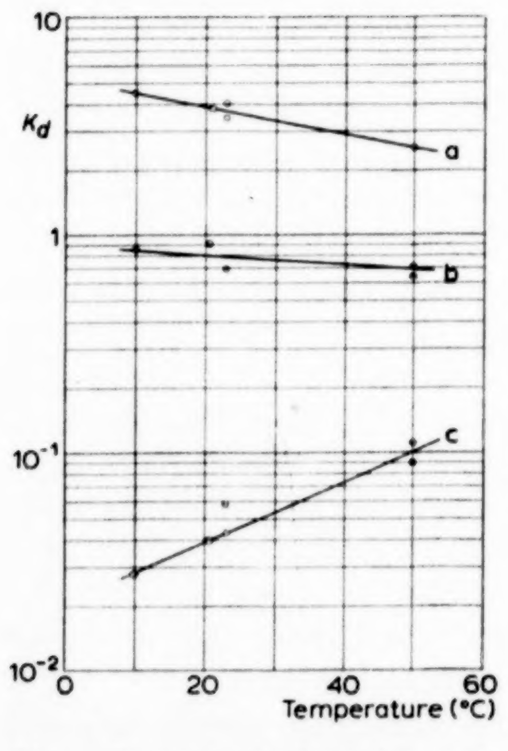

Fig. 2. Temperature dependence of $K_d$ values. a, 10 $M$ $HNO_3$ in aqueous phase; b, 5 $M$ $HNO_3$ in aqueous phase; c, 1 $M$ $HNO_3$ in aqueous phase.

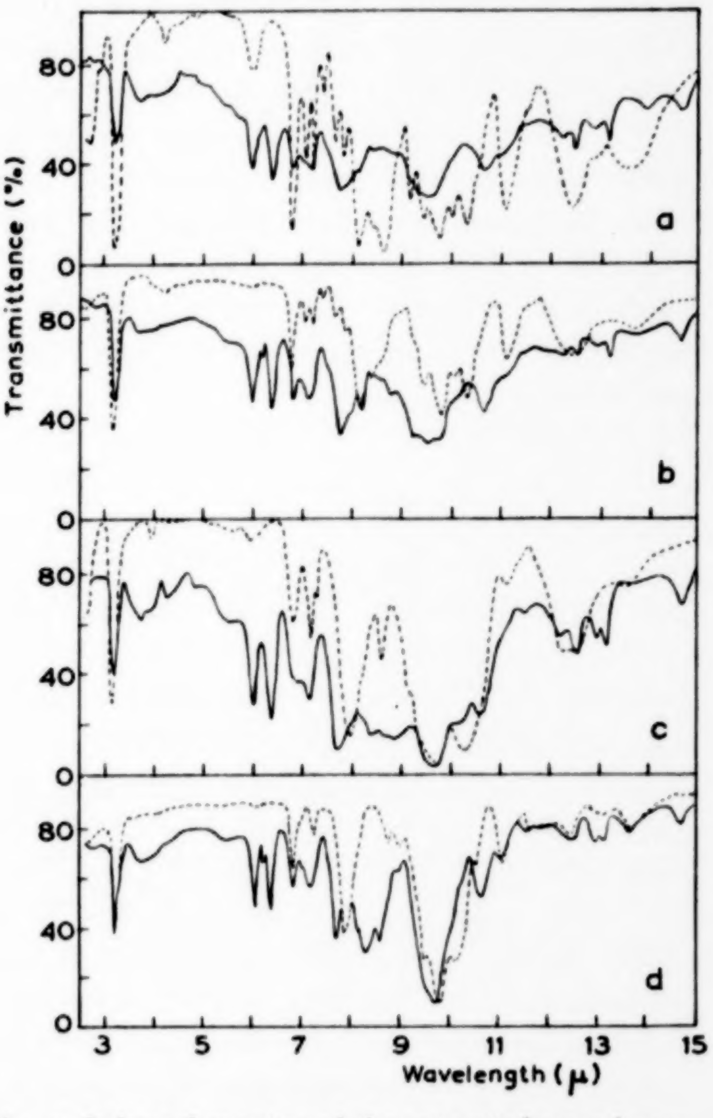

Fig. 3. Infrared spectra of the extracted complexes. a, —— Zr + tri-*n*-butyl phosphine oxide, ---- tri-*n*-butyl phosphine oxide; b, —— Zr + tri-*n*-butyl phosphinate, ---- tri-*n*-butyl phosphinate; c, —— Zr + diethyl butyl phosphonate, ---- diethyl butyl phosphonate; d, —— Zr + tri-*n*-butyl phosphate, ---- tri-*n*-butyl phosphate.

The observation of the infrared spectra supports the evidence of covalent complex formation between zirconium and organophosphorus solvents.

## ACKNOWLEDGEMENTS

The authors express their appreciation to Drs. KENJIRO KIMURA, TAKASHI MUKAIBO, KEICHI OSHIMA AND KEIJI NAITO for their suggestions and encouragement. The authors are also grateful to Mr. HIDEO KAMIYAMA for the interpretation of the infrared spectra, and to Dr. RYOICHI UEHARA of Tama Chemical Co. for the synthesis of the organophosphorus solvents.

## SUMMARY

The extraction of zirconium from nitric acid media with alkyl phosphates, phosphonate, phosphinate and phosphine oxide was studied. The extraction ability is affected by alkyl substituents attached to the phosphoryl group as well as by the solvent structure, the order of efficiency being: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec* -butyl phosphate > diethyl butyl phosphate > normal alkyl phosphates. In the extraction with normal alkyl phosphates, two solvent molecules and four nitrate ions combine with one atom of zirconium. The equilibrium constant and the effect of temperature were studied in the extraction with tri-*n*-butyl phosphate. The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with the organophosphorus solvents were measured; it was confirmed that a covalent complex was formed.

## RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du zirconium, au moyen de solvants organophosphorés, en milieu nitrique. Ils ont examiné en particulier l'extraction à l'aide de tributylphosphate.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Zirkonium mit organischen Phosphorverbindungen, besonders Tributylphosphat.

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# SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH STANNOUS IODIDE REAGENT

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(Received February 6th, 1961)

AYRES *et al.*[1] and others[2] have reported on the use of a tin(II) chloride reagent for the spectrophotometric determination of rhodium. The method is simple and reproducible but lacks sensitivity. BERMAN AND IRONSIDE[3] have reported on the use o-tin(II) bromide in hydrobromic acid as the color developing agent for rhodium analyfsis. Recently, PANTANI AND PICCARDI[4] have studied the behavior of Rh, Pt, Pd and Au ions with tin(II) bromide both in aqueous solutions and in isoamyl alcohol extracts. The tin(II) bromide method for rhodium is more sensitive than the tin(II) chloride method but it requires a redistillation of hydrobromic acid and the use of perchloric acid as a color stabilizing agent. Each method has serious interferences from other transition metals which necessitates the separation of rhodium from these elements before an analysis.

This study was undertaken to explore the possibility that a tin(II) iodide reagent might be more sensitive to rhodium than either the tin(II) chloride or bromide reagent. The development of such a method is described below.

## EXPERIMENTAL

### *Apparatus and reagents*

The spectra were recorded with a Beckman DK-1 spectrophotometer. Individual absorbancy measurements were made with a Beckman DU spectrophotometer using 1-cm quartz cells.

Rhodium(III) solutions were prepared by dissolving the trichloride in 0.3 *N* hydrochloric acid and standardizing by the method of GILCHRIST[5].

Tin(II) chloride solutions were prepared by dissolving 2 parts by weight of $SnCl_2 \cdot 2\,H_2O$ in 1 part by volume of concentrated hydrochloric acid and diluting with 5 parts by volume of distilled water. For acidity calculations this solution was considered 2 *N* in hydrochloric acid. Tin metal was placed in the stock solution.

All other reagents were of analytical grade and were used as indicated.

### *Recommended procedure*

Transfer the rhodium(III) sample to a 25-ml volumetric flask. Add sufficient hydrochloric acid so that the final solution will be 1 *N* in hydrochloric acid. Add 5 ml of 20% (w/v) potassium iodide solution, mix, and heat for 15 min in a boiling waterbath.

Cool to room temperature. Pipet 5 ml of the stannous chloride solution into the flask and dilute to volume with distilled water. Mix and heat the unstoppered flasks for 2 min in a boiling waterbath. Cool immediately to room temperature in an ice bath. Measure the absorbancy of the solution at 460 m$\mu$ *vs.* a blank prepared identically to the sample except for the omission of rhodium. Determine the rhodium concentration from a standard curve.

### *Effect of temperature on solution absorbancy*

Time studies indicated that the sample must be heated with potassium iodide in a boiling waterbath for at least 8–10 min to convert the rhodium chloride complex to a reproducible iodide complex; 15 min heating was accepted as routine to insure a complete conversion with each sample. Upon the addition of tin(II) chloride to the sample containing the rhodium iodide complex a rose colored solution is formed which rapidly changes to a golden brown. At room temperature the absorbancy increases continuously for 18 h and then decreases. A 2-min heating period, however, produces a solution whose color is stable for at least 24 h and which exhibits an absorption maximum at 460 m$\mu$. The time of heating is not critical; heating periods up to 5 min do not alter the results. The spectral curve is shown in Fig. 1.

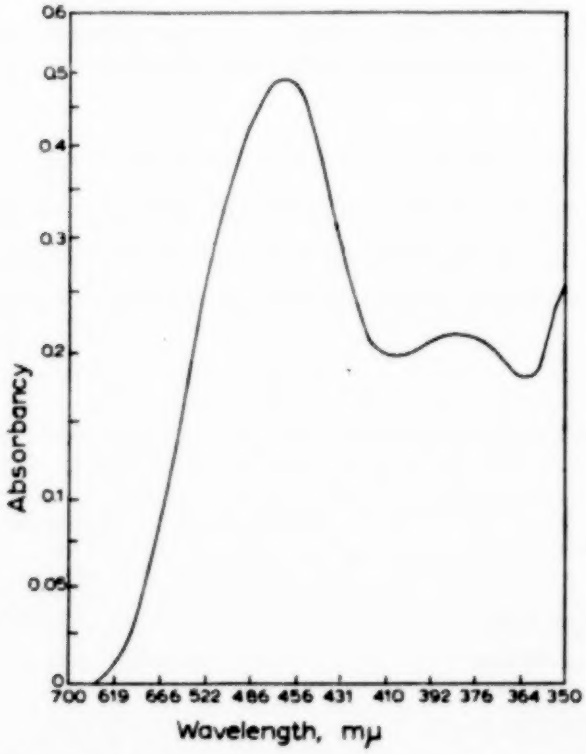

Fig. 1. Absorption spectra of rhodium–tin(II) iodide complex.

### *Effect of hydrochloric acid concentration on solution absorbancy*

The molar absorptivity of the rhodium complex increases with a decrease in acid concentration as shown in Fig. 2. The lowest practical acidity is about 1 *N* due to the precipitation of $SnI_2$ in solutions below this acidity. The acid concentration of the final solution is somewhat critical since the absorbancy changes 0.01 units for each 0.1 *N* increment in solution acidity for a solution with an absorbancy of about 0.5. The precision of the method indicates, however, that acidity control is easily effected.

### *Effect of potassium iodide concentration on solution absorbancy*

The absorbancy increases as the volume of iodide solution added approaches 5 ml but remains constant for greater volumes of reagent. Large excesses of iodide reagent must be avoided to prevent the precipitation of $SnI_2$. A precipitate forms if as much as 11 ml of reagent are added.

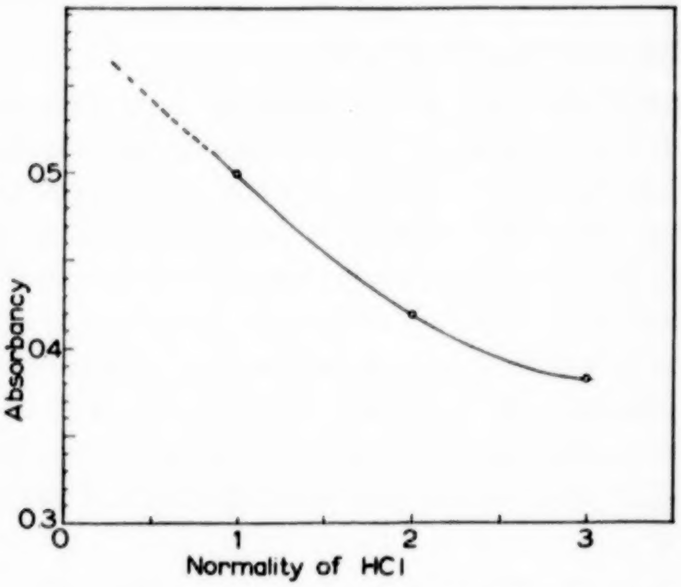

Fig. 2. Variation of absorbancy of rhodium–tin(II) iodide complex at 460 mμ with changes in hydrochloric acid concentration.

### *Effect of tin(II) chloride concentration on solution absorbancy*

Variations from 40 to 200% of the prescribed amount of tin(II) chloride produce only a small increase (10%) in absorbancy if the hydrochloric acid content is maintained constant. 5 ml of reagent were chosen as a practical upper limit.

TABLE I

CONCENTRATION OF INTERFERENCES NECESSARY TO GIVE A 1% VARIATION IN SAMPLE ABSORBANCY FOR A 2 p.p.m. Rh(III) SOLUTION

| *Interfering ion* | *Concentration in p.p.m.* | *Direction of change* |
|---|---|---|
| Co as $CoCl_2$ | 7 | + |
| Sb as $SbCl_3$ | 1 | + |
| Ti as $TiCl_4$ | 8 | — |
| Cu as $CuCl_2$ | 5 | + |
| Fe as $FeCl_3$ | 10 | + |
| Ni as $NiCl_2$ | 20 | + |
| Cr as $CrCl_3$ | 10 | + |
| Ir as $IrCl_3$ | 0.08 | + |
| Pd as $PdCl_2$ | 3 | ppt. forms |
| Pt as $PtCl_2$ | 0.1 | + |
| $I_2$ | 280 | + |
| $Na_2SO_4$ | 11,000 | + |
| NaCl | 3,300 | — |
| $H_2SO_4$ | 50,000 | — |

### *Effect of diverse ions, salts and sulfuric acid on solution absorbancy*

The more common interferences and the amounts that can be tolerated by the procedure are listed in Table I. Note that other platinum group metals and transition metals interfere seriously.

The positive effect of sodium sulfate is probably due to a decrease in hydrochloric acid concentration by the metathetical formation of unionized $HSO_4^-$.

Small amounts of iodine are formed during the first heating period, presumably due to dissolved oxygen in the distilled water and reagents. This does not affect the reproducibility of the method as can be seen from the following. The absorbancy of the blank is increased by only 0.006 units if 50 mg (2000 p.p.m.) of free iodine are added but the effect on the sample is more pronounced. 280 p.p.m. of iodine can be tolerated without causing an error in the absorbancy measurement greater than 1%. Consequently the solutions must be free of oxidizing agents in amounts sufficient to produce an iodine concentration of 280 p.p.m.

### *Optimum working range*

The Ringbom plot (Fig. 3) shows the reliable working range to be from 0.4 to 3 p.p.m. Rh. The system obeys Beer's law and has a molar absorptivity of $3.9 \cdot 10^4$ at 460 m$\mu$.

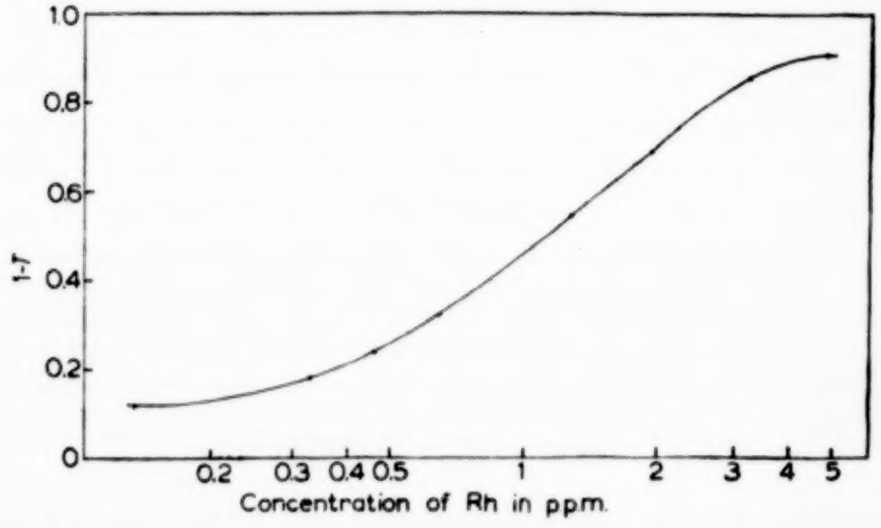

Fig. 3. Ringbom plot of rhodium–tin(II) iodide complex determined at 460 m$\mu$.

### *Precision of method*

6 samples containing 2 p.p.m. of Rh(III) were analyzed on three different days giving an average deviation of 0.3% and a standard deviation of 0.4%.

## DISCUSSION

A choice among the tin(II) halide reagents for the determination of rhodium may rest upon the sensitivity desired, the iridium and nickel content of the sample, the analyst's aversion to the use of perchloric acid, the cost and redistillation of hydrobromic acid, the greater stability of $SnCl_2$ in hydrochloric acid than in hydrobromic acid, and knowledge of the acid content of the sample. All three reagents produce stable and reproducible colors with rhodium and the analytical procedures are simple and not very different.

The molar absorptivities of the rhodium–tin(II) chloride[1], rhodium–tin(II) bromide[3], and rhodium–tin(II) iodide complexes are $3.9 \cdot 10^3$, $2.9 \cdot 10^4$ and $3.9 \cdot 10^4$ respectively.

Except for the lower sensitivity which often may be satisfactorily increased simply by using absorption cells of longer path length, the stannous chloride reagent appears to be superior to both the bromide and iodide reagent. The tin(II) chloride method has the greatest tolerance for iridium (45 : 1) and nickel ions.

For samples requiring a greater sensitivity the choice of methods lies between the use of the bromide or iodide reagents. The bromide method appears to tolerate more iridium than the iodide method although different tolerances are reported[3,4]. The iodide method appears to be slightly more sensitive to changes in acid concentration than the bromide method.

All three halide methods are subject to serious interferences from other platinum group metals and numerous other transition metals. The difficulty can be eliminated only by the prior separation of rhodium from the sample.

The chief advantages of the tin(II) iodide method are its sensitivity, lack of dependence on perchloric acid for stability, and its use of cheaper and more easily prepared reagents.

## ACKNOWLEDGEMENT

We gratefully acknowledge the financial support given this program by Celanese Corporation of America.

## SUMMARY

The tin(II) iodide reagent reacts with rhodium to form a stable colored complex with an absorption maximum at 460 mμ. The system obeys Beer's law and exhibits a molar absorptivity of $3.9 \cdot 10^4$ at 460 mμ. Rhodium concentrations between 0.4 and 3 p.p.m. can be determined with an average deviation of only 0.3%. The method compares favorably with the tin(II) chloride and bromide methods for rhodium and is considerably more sensitive. Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni and Fe interfere with the method. Consequently, just as is the case with the chloride and bromide reagent, Rh must be separated from most samples prior to an analysis.

## RÉSUMÉ

L'iodure d'étain(II) est proposé comme réactif pour le dosage spectrophotométrique du rhodium. La sensibilité est beaucoup meilleure que celle obtenue avec les chlorure et bromure d'étain(II). Les éléments Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni et Fe gènent également.

## ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Rhodium ist als Komplexbildner das Zinn-(II)-jodid besser geeignet als Zinn-(II)-chlorid oder -bromid. Die störenden Elemente Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni und Fe müssen vorher entfernt werden.

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# REFERENCE ELECTRODES FOR VOLTAMMETRY IN ACETONITRILE

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(Received January 25th, 1961)

Over the past few years interest in acetonitrile as a polarographic solvent has produced some extremely fruitful results. These studies have developed some ambiguities with regard to reference electrodes for acetonitrile polarography. Recently when one of the authors attempted to convert the data of several workers to a common reference electrode (aqueous saturated calomel), it became apparent that it was not clear how the individual reference electrodes had been used.

In general, reference electrodes for acetonitrile have been either the ordinary aqueous saturated calomel or the silver ion-silver system used by PLESKOV[1] in potentiometric measurements. PLESKOV measured potentials of various metal-metal ion couples in acetonitrile using a half-cell of $AgNO_3(0.01\ M)$, $CH_3CN/Ag$ as the reference. KOLTHOFF AND COETZEE[2] preferred the aqueous saturated calomel electrode but compared their data to PLESKOV's reference apparently by measuring the system $AgNO_3(0.01\ M)$, Ag $\|$ S.C.E. aq. They reported the silver ion-silver electrode to be $+0.29$ V *vs.* S.C.E. aq. However, if it is assumed that their polarographic $E_{1/2}$ for silver ion reduction in 0.1 $M$ sodium perchlorate medium (0.32 V *vs.* S.C.E.) can be identified as usual with $E°$ for silver ion-silver, then $E_{Ag^+(0.01\ M),\ Ag}$ *vs.* S.C.E.aq. would be $+0.20$ V. This appears inconsistent with the value $+0.29$ V. On the other hand, the $E_{1/2}$ for silver ion reduction in 0.1 $M$ tetraethylammonium perchlorate reported by LARSON AND IWAMOTO[3] ($+0.42$ V *vs.* S.C.E.), when converted to $E_{Ag^+(0.01\ M),\ Ag}$ gives $+0.30$ V *vs.* S.C.E. aq.

POPOV AND GESKE[4] developed a silver-silver chloride electrode where the solubility of silver chloride in acetonitrile was controlled by a fixed concentration of tetramethylammonium chloride. Again the data were converted to PLESKOV's $Ag^+(0.01\ M)/Ag$ reference using the value $+0.29$ V. In more recent acetonitrile work, GESKE[5,6] has used the aqueous saturated calomel as the actual reference electrode.

LARSON AND IWAMOTO, in fundamental studies of solvent effects on metal ion reductions, used the aqueous saturated calomel electrode but did not make conversions to the silver ion-silver system[3]. Similarly KUWANA[7], as well as VOORHIES AND FURMAN[8], studied anodic oxidations in acetonitrile using the aqueous saturated calomel.

LUND[9], in pioneering studies of the oxidation of hydrocarbons in acetonitrile, used as a reference electrode what has been tacitly assumed to be the silver ion-silver system of PLESKOV. His reference actually was $AgClO_4(0.1\ M)$, $NaClO_4(0.5\ M)$, Ag.

Since the aqueous saturated calomel does function satisfactorily in acetonitrile polarography (the effect of leakage through the usual salt bridge is easily minimized by working with an H-type cell where any drainage is kept from contact with the actual polarographic medium), it would seem very desirable to convert all existing $E_{1/2}$ values in acetonitrile to the aqueous saturated calomel reference. This is in keeping with polarographic practice where, in aqueous media, it is rare indeed that any reference other than saturated calomel is used today. Due to the uncertainties in the nature of the silver ion–silver reference systems, a series of such reference electrodes have been measured *vs.* an aqueous saturated calomel electrode. The data indicate that care must be exercised in converting from one reference to the other.

## EXPERIMENTAL

Potential measurements were made with an H-type cell separated by a porous frit. One compartment (side A) was filled with an acetonitrile silver salt system and the other (side B) with an acetonitrile solution of either lithium, sodium, or tetraethylammonium perchlorate. An aqueous S.C.E. was immersed in side B and a heavy silver foil in side A. Several different calomel and silver foil electrodes were used. Potential measurements were made with a Rubicon Model 2730 potentiometer. Table I summarizes the data obtained with the various cells. Each observed voltage is the average of at least two measurements with different silver foils. The differences between these measurements were never greater than 2 mV. Especially in the case where the aqueous saturated calomel dipped into the 0.5 *M* sodium perchlorate medium, some precipitation occurred on the outside of the salt bridge tip and it is felt that the accuracy of these measurements is about ± 2 mV. For convenience of discussion, the various cells are numbered in Table I as indicated.

TABLE I

VARIOUS $Ag^+/Ag$ REFERENCE ELECTRODES IN ACETONITRILE *vs.* S.C.E. aq.

| *Cell No.* | *Side "A"* | *Side "B"* | *E(V)* |
|---|---|---|---|
| | *$LiClO_4$* | | |
| 1 | 0.1 *M* $AgNO_3$ | 0.1 *M* $LiClO_4$ | 0.305 |
| 2 | 0.1 *M* $AgNO_3$, 0.1 *M* $LiClO_4$ | 0.1 *M* $LiClO_4$ | 0.320 |
| 3 | 0.1 *M* $AgNO_3$, 0.5 *M* $LiClO_4$ | 0.5 *M* $LiClO_4$ | 0.308 |
| 4 | 0.01 *M* $AgNO_3$ | 0.1 *M* $LiClO_4$ | 0.259 |
| 5 | 0.01 *M* $AgNO_3$, 0.1 *M* $LiClO_4$ | 0.1 *M* $LiClO_4$ | 0.267 |
| | *$NaClO_4$* | | |
| 6 | 0.1 *M* $AgNO_3$ | 0.1 *M* $NaClO_4$ | 0.301 |
| 7 | 0.01 *M* $AgNO_3$ | 0.1 *M* $NaClO_4$ | 0.253 |
| 8 | 0.1 *M* $AgClO_4$, 0.5 *M* $NaClO_4$ | 0.5 *M* $NaClO_4$ | 0.301 |
| | *$Et_4NClO_4$* | | |
| 9 | 0.1 *M* $AgNO_3$ | 0.1 *M* $Et_4NClO_4$ | 0.336 |
| 10 | 0.1 *M* $AgNO_3$, 0.1 *M* $Et_4NClO_4$ | 0.1 *M* $Et_4NClO_4$ | 0.337 |
| 11 | 0.01 *M* $AgNO_3$ | 0.1 *M* $Et_4NClO_4$ | 0.291 |
| 12 | 0.01 *M* $AgNO_3$, 0.1 *M* $Et_4NClO_4$ | 0.1 *M* $Et_4NClO_4$ | 0.291 |
| | *No supporting electrolyte* | | |
| 13 | 0.1 *M* $AgNO_3$ | 0.1 *M* $AgNO_3$ | 0.337 |
| 14 | 0.01 *M* $AgNO_3$ | 0.01 *M* $AgNO_3$ | 0.300 |

## DISCUSSION

Unless the aqueous saturated calomel reference electrode is immersed directly in a 0.01 $M$ acetonitrile solution of silver ion, it does not appear possible to determine definitively the value of PLESKOV's reference electrode, $AgNO_3(0.01)$, Ag, $CH_3CN$, *vs.* S.C.E. aq. As the data in Table I show, the potential difference between PLESKOV's reference electrode and an aqueous saturated calomel electrode is affected quite markedly by the nature of the electrolyte solution in which the aqueous saturated calomel electrode is immersed (See cells No. 4, 7, 11 and 14). With 0.1 $M$ acetonitrile solutions of sodium perchlorate and lithium perchlorate as the electrolyte solution, $E_{\text{PLESKOV's electrode}}$ *vs.* the aqueous saturated calomel is close to +0.26 V. With 0.1 $M$ acetonitrile solution of tetraethylammonium perchlorate, $E_{\text{PLESKOV's electrode}}$ *vs.* aqueous saturated calomel is +0.291 V, a value which agrees closely with that reported by KOLTHOFF AND COETZEE[2]. This potentiometric value of +0.291 V *vs.* S.C.E. aq. agrees closely with the value +0.30 V *vs.* S.C.E. aq. derived from polarographic data. The potentiometric value of +0.26 V *vs.* S.C.E. where sodium perchlorate and lithium perchlorate were involved, however, is not consistent with the polarographic data for silver ion reduction in sodium perchlorate. The interesting effect of sodium perchlorate and lithium perchlorate, on one hand, and tetraethylammonium perchlorate, on the other, has been observed by LARSON AND IWAMOTO[3]. They observed shifts in $E_{1/2}$ values for the reduction of metal ions when the concentration of lithium perchlorate, the supporting electrolyte, was varied, whereas variation of the concentration of tetraethylammonium perchlorate, however, had no effect on the $E_{1/2}$ values[10]. This difference in behavior between the two alkali perchlorates and tetraethylammonium perchlorate is probably due to a difference in the nature of the "solvated" cations. Lithium and sodium ions probably are appreciably solvated and to about the same extent, while the tetraethylammonium ion is not. The potential measurements with tetraethylammonium perchlorate and of cells 13 and 14, which contain no supporting electrolyte, appear to bear out such an interpretation. Thus the value of PLESKOV's reference electrode *is* +0.30 V *vs.* S.C.E. aq.

Since LUND carried out his electrochemical studies in 0.5 $M$ acetonitrile solution of sodium perchlorate, *i.e.*, a cell identical with No. 8 in Table I, conversion of his $E_{1/2}$ values to the aqueous saturated calomel reference does not present any problem.

It is interesting to note that a tenfold change in silver ion concentration does not give quite the theoretical 0.059 change in $E_{Ag^+, Ag}$. The values fall between 0.045 and 0.053.

## ACKNOWLEDGEMENT

This work was supported in part by the Atomic Energy Commission through contract AT(11-1)-686 and in part by Petroleum Research Fund Grant 662-A, and this support is gratefully acknowledged.

## SUMMARY

The saturated calomel electrode is *the* reference electrode in aqueous polarographic studies. Such is not the case, however, with nonaqueous polarographic studies. In particular acetonitrile has been used as the solvent for many polarographic studies with just as many reference electrodes. An attempt has been made to correct this unfortunate situation. Appropriate measurements have been made to evaluate the potential of the various reference electrode systems used in acetonitrile with respect to the aqueous saturated calomel electrode.

## RÉSUMÉ

Au cours de leurs recherches de polarographie en milieux nonaqueux (en particulier dans l'acétonitrile), les auteurs ont effectué des mesures appropriées pour déterminer le potentiel de divers systèmes de référence, par rapport à l'électrode aqueuse à calomel saturée.

## ZUSAMMENFASSUNG

Beschreibung von Untersuchungen über die Polarographie in nicht-wässrigem Medium, besonders Acetonitril. Es wurden die Potentiale verschiedener Referenz-elektrodensysteme in Acetonitril bestimmt und mit der Kalomelelektrode verglichen.

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# APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

## II. TIN-BASE ALLOYS

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(Received October 1st, 1960)

### *Solders*

Besides lead and tin, solders may also contain antimony (1–2%) and several impurities like copper, arsenic, etc. Even when tin is the base metal, the analytical methods for antimony, lead and tin are the same as those described in Part I for the lead-base alloys[1]. Copper may be determined by the methods described in an earlier paper[2].

### *Bearing alloys*

*(a) Separate analysis of antimony and subsequent determination of copper and lead.* In tin-base bearing alloys, while antimony and copper are present in quantities that may be determined with accuracy on a 1-g sample, lead is quite frequently present in small percentages which do not allow an exact determination by cathodic deposition from a 1-g alloy sample. For this reason, a separate controlled potential electrolytic

method was described by which the determination of copper and lead is made on a 5-g weighed sample[2]. In such a case, antimony must be assessed on another sample of the alloy and the method already described[1] for lead-base alloys may be followed.

*(b) Successive determination of antimony, copper and lead.* When lead is not less than 1%, the 1-g sample is sufficient for an accurate determination and successive deposition of antimony, copper and lead may be done. Antimony is titrated with bromate according to the method already described for lead-base alloys[1]; then 5 g of tartaric acid, 2 g of succinic acid, 1 g of hydrazine dihydrochloride are added to the solution and the pH is brought to 5–5.2 with ammonia. Any adjustments of the pH, if required, may be done with 1 : 1 hydrochloric acid and ammonia. Copper is deposited between —0.30 and —0.40 V *vs.* S.C.E. and, after weighing the copper, lead is deposited on the copper-plated cathode between —0.60 and —0.65 V *vs.* S.C.E.

In this case, bismuth and silver, which are almost always present in very small percentages, are determined together with the copper. Table I gives the results of the successive determination of antimony, copper and lead on standard sample 54c (N.B.S.). The values found agree quite well with the certified percentages.

With slight modifications to the method, the synthetic solutions indicated in Table II were analyzed. Since the dissolution of copper together with the other metals by sulfuric acid proved quite difficult, these solutions were prepared by dissolving copper and lead in 1 : 1 nitric acid and evaporating twice to white fumes with sulfuric acid; after cooling, antimony, tin and 2 g of potassium pyrosulfate were added followed by the usual attack already described[1] in Part I.

TABLE I

DETERMINATIONS ON SAMPLE 54c (N.B.S.) — TIN-BASE BEARING METAL

| *Composition* | | | *Weighed* *g* | *Found* *g* | | |
|---|---|---|---|---|---|---|
| | | | | *Sb(+As)* | *Cu* | *Pb* |
| Cu = 4.30 | Sb = 7.28 | As = 0.049 | 1 | 7.35 | 4.31 | 1.98 |
| Bi = 0.028 | Pb = 1.99 | Fe = 0.033 | 1 | 7.36 | 4.30 | 1.99 |
| Ag = 0.02 | Sn = 86.29 | Ni = 0.012 | 1 | 7.34 | 4.31 | 2.02 |
| | | | 1 | 7.33 | 4.32 | 2.00 |

TABLE II

DETERMINATION ON SYNTHETIC SOLUTIONS

| *No.* | *Sb (g)* | | *Cu (g)* | | *Pb (g)* | | *Sn (g)* |
|---|---|---|---|---|---|---|---|
| | *Weighed* | *Found* | *Weighed* | *Found* | *Weighed* | *Found* | *Weighed* |
| 1 | 0.1497 | 0.1494 | 0.0233 | 0.0235 | 0.1085 | 0.1088 | 0.7518 |
| 2 | 0.1490 | 0.1494 | 0.0208 | 0.0211 | 0.1138 | 0.1132 | 0.7700 |
| 3 | 0.1566 | 0.1569 | 0.0248 | 0.0250 | 0.2029 | 0.2027 | 0.6606 |
| 4 | 0.1531 | 0.1527 | 0.0244 | 0.0244 | 0.2001 | 0.1999 | 0.6783 |

In the analyses of solutions 1 and 2, 8 g of tartaric acid were used instead of 5 g, but otherwise the procedure was unchanged; for solutions 3 and 4 the tartaric acid used also amounted to 8 g but this time, owing to the difficulty of dissolving all the lead sulfate present at pH 5, the pH value was brought to 7.2 before the copper was deposited at —0.45 to —0.50 V *vs.* S.C.E.; this was followed by the deposition of lead on the copper-plated cathode at —0.60 to —0.65 V *vs.* S.C.E. with an initial pH of 7.2 for 15–20 min; subsequently the pH was corrected to about 5 at which value the deposition ended; in accordance with the method described for lead-base alloys[1].

*(c) Determination of tin.* Some tests have been run on the electrolytic deposition of tin from the solution resulting after titration of antimony and after electrolysis of copper and lead following the procedure outlined in Part I for tin in lead-base alloys. Tin deposits completely but a partial co-deposition of antimony is unavoidable. This co-deposition starts when most of the tin is already deposited. The following results were obtained, for instance, with sample 54c whose composition is given in Table I: Sn% = 86.63, 86.46, 86.70, 86.94, 86.56.

Other tests performed to obtain a satisfactory successive electrodeposition of tin also gave more or less unfavorable results. In alloys which contain tin as the base metal, tin may be computed by difference, but quite often a direct determination is desirable. Since a rapid successive deposition method could not be developed, the following separate procedure was devised; this is also applicable to lead-base alloys.

### METHOD

In a 400-ml tall-form beaker, dissolve 1 g of alloy with 15 ml of sulfuric acid and 2 g of potassium pyrosulfate as described in Part I. Slowly and cautiously, add 20 ml of 1 : 1 hydrochloric acid, dilute to 100 ml with distilled water and boil for 1–2 min while stirring with a glass rod. Dissolve the lead sulfate while heating by adding a slight excess of 1 : 1 hydrochloric acid so that during the subsequent cooling, the precipitate will either be absent or negligible; if lead is present in very low percentages hydrochloric acid need not be added at all, while 50 ml of the acid are required for about 0.2 g of lead and 70 ml for about 0.8 g of lead. To the hot solution (85–95°) then add 0.3 g of hydrazine dihydrochloride; dilute as much as required to keep the electrodes submerged and electrolyze at —0.30 V *vs.* S.C.E., starting at a more negative cathode potential so as not to exceed, initially, a current intensity of 0.6–0.8 A. During electrolysis, while the solution cools, some lead sulfate may deposit on the gauze but this does not interfere. This preliminary electrolysis serves to separate antimony and part of the copper present; when it is ended, wash the electrodes and the deposited lead sulfate, if any, well with distilled water. Oxidize the solution with potassium permanganate powder up to pink or yellow and then decolorize with some hydrazine dihydrochloride. Add 8 g of tartaric acid and then concentrated ammonia to give pH 7–7.2: a small residue may remain undissolved (apparently due to the presence of manganese) but it does not interfere since it re-dissolves during electrolysis. Then add 2 g of succinic acid and 1 g of hydrazine dihydrochloride, adjust the pH with ammonia and 1 : 1 hydrochloric acid to about 5 and deposit lead at a final cathode potential of —0.65 V *vs.* S.C.E. If lead is greater than 0.2 g, adjust the pH to 7–7.2, deposit lead at a final cathode potential of —0.65 V *vs.* S.C.E. and then correct the pH to about 5 as described in Part I.

To check the pH narrow range test papers will do. Neutralization with ammonia heats the solution but it may be electrolyzed even if warm.

After electrolysis of lead, acidify the solution with 40 ml of concentrated hydrochloric acid, add 0.3 g of hydrazine dihydrochloride and deposit tin at —0.65 V *vs.* S.C.E. according to the procedure outlined previously[1].

## RESULTS

The method described was first tested on sample No. 54c (N.B.S.), the composition of which is given in Table I, and the percentages found, indicated in Table III, are mostly within ±0.05%, the maximum deviation being ±0.1%.

Some synthetic solutions were then prepared with the addition of lead and antimony — as metals — to the No. 54c sample, as shown in Table IV. In this case results were again excellent.

TABLE III

SAMPLE NO. 54C — TIN-BASE BEARING METAL

| *Sn %* | | | | |
|---|---|---|---|---|
| 86.35 | 86.20 | 86.24 | 86.33 | 86.20 |
| 86.32 | 86.29 | 86.24 | 86.26 | 86.34 |
| 86.22 | 86.24 | 86.25 | 86.25 | 86.31 |
| 86.33 | 86.29 | 86.36 | 86.38 | |

TABLE IV

DETERMINATION OF TIN IN SYNTHETIC SOLUTION

| *No.* | *Sb* | *Pb* | *54c* | *Sn* | *Sn* |
|---|---|---|---|---|---|
| | *Weighed* g | *Weighed* g | *Weighed* g | *Calculated* g | *Found* g |
| 1 | 0.0980 | 0.2031 | 0.8177 | 0.7056 | 0.7052 |
| 2 | 0.1012 | 0.2068 | 0.8230 | 0.7102 | 0.7108 |
| 3 | 0.0993 | 0.3039 | 0.8302 | 0.7164 | 0.7159 |
| 4 | 0.1028 | 0.2067 | 0.8225 | 0.7097 | 0.7086 |
| 5 | 0.1015 | 0.1970 | 0.8238 | 0.7108 | 0.7108 |
| 6 | 0.1017 | 0.2168 | 0.8047 | 0.6943 | 0.6946 |
| 7 | 0.1048 | 0.1108 | 0.8010 | 0.6911 | 0.6911 |
| 8 | 0.1026 | 0.2345 | 0.8048 | 0.6945 | 0.6944 |
| 9 | 0.1040 | 0.1041 | 0.8223 | 0.7096 | 0.7097 |
| 10 | 0.1036 | 0.1031 | 0.8057 | 0.6952 | 0.6952 |

TABLE V

MIXED SAMPLES, DETERMINATION OF TIN

| *No.* | *53d* | *54c* | *Sb* | *Cu* | *Sn* | *Sn* |
|---|---|---|---|---|---|---|
| | *Weighed* g | *Weighed* g | *Weighed* g | *Added* g | *Calculated* g | *Found* g |
| 1 | 1.000 | — | — | — | 0.0494 | 0.0489 |
| 2 | 1.000 | — | 0.0503 | — | 0.0494 | 0.0490 |
| 3 | 1.000 | — | 0.1049 | — | 0.0494 | 0.0491 |
| 4 | 1.000 | — | 0.0508 | 0.0500 | 0.0494 | 0.0487 |
| 5 | 0.1951 | 0.6994 | 0.0977 | — | 0.6127 | 0.6133 |
| 6 | 0.5040 | 0.5025 | 0.1040 | — | 0.4585 | 0.4586 |
| 7 | 0.5004 | 0.5031 | 0.1004 | — | 0.4589 | 0.4581 |
| 8 | 0.7549 | 0.2482 | 0.1042 | — | 0.2515 | 0.2510 |
| 9 | 0.7031 | 0.2392 | 0.1006 | — | 0.2406 | 0.2505 |
| 10 | 0.9002 | 0.1003 | 0.1033 | — | 0.1310 | 0.1309 |
| 11 | 0.8979 | 0.1016 | 0.0769 | — | 0.1319 | 0.1318 |

To test the method on lead-base alloys, recourse was had to mixtures of samples No. 54c and 53d to which were also added antimony as metal before sample dissolution, and copper as copper sulfate pentahydrate after dissolution and dilution. In all cases, as shown by Table V, the results were satisfactory. The composition of sample No. 53d is as follows: Sb 9.92%, Sn 4.94%, Cu 0.268%, Bi 0.135%, As 0.045%, Ni 0.02%, Pb (by difference) 84.69%.

The method described offers remarkable investigation possibilities for lead- and tin-base alloys. According to SCHOCH AND BROWN[3] antimony may be separated from copper, in a hydrochloric acid solution, by electrolyzing at 70° at a cathode potential of −0.40 V *vs.* S.C.E. On the other hand, at 70°–80° and in the presence of hydrochloric acid, a lot of lead sulfate may be kept in the solution. It is therefore probable that further investigations might lead to a new procedure for the successive and quantitative electrolytic separation of antimony, copper, lead and tin.

## ACKNOWLEDGEMENTS

The author wishes to thank Dr. A. ZAZZARONI, Director of the FIAT Laboratories, and Dr. Ing. C. F. BONA, Director of FIAT's L.R.C.A.A., for permission to publish this paper, Dr. S. BERTOLDI for his encouragement and Mr. P. GIACCONE for his efficient cooperation.

## SUMMARY

Electrodeposition methods are described for the determination of antimony, copper and lead in tin-base alloys and a method for the determination of tin by controlled-potential electrolysis is discussed.

## RÉSUMÉ

Une méthode est décrite pour le dosage de l'étain par électrolyse à potentiel contrôlé. L'auteur a examiné également le dosage de l'antimoine, du cuivre et du plomb dans des alliages à base d'étain.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Zinn, Antimon, Kupfer und Blei in Zinnlegierungen durch Elektrolyse mit kontrolliertem Potential.

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# POLAROMETRIC DETERMINATION OF AROMATIC ALDEHYDES WITH 2,4-DINITROPHENYLHYDRAZINE

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(Received January 19th, 1961)

Several indirect analytical methods are available for the determination of carbonyl compounds, most of which utilize additive or condensation properties of these compounds. Direct volumetric determinations are less common, because carbonyl compounds are mostly neutral substances, which eliminates the possibility of acid-base titrations, and oxidation-reduction reactions with common agents occur too slowly to be useful for direct titrations. We have already reviewed the possibilities for the titration of carbonyl compounds[1]. An evaluation of analytical methods from a unified theoretical point of view has recently been given by BUDĚŠÍNSKÝ[2].

2,4-Dinitrophenylhydrazine (DNPH) is most frequently used for the determination of carbonyl compounds. Its solutions in 2 *N* hydrochloric acid are stable, and with a number of carbonyl compounds it forms readily crystallising 2,4-dinitrophenylhydrazones:

$$>C = O + NH_2NHC_6H_4(NO_2)_2 \rightarrow >C = NNH_2C_6H_4(NO_2)_2 + H_2O$$

In an indirect determination, in which the sample was treated with an excess of this reagent, which was then determined oxidimetrically[3] with chloramine-T we observed that some aromatic aldehydes reacted with DNPH so rapidly that this reaction could be used for a direct titration.

ZOBOV, LIALIKOV *et al.*[4,5] have studied this problem and titrated certain carbonyl compounds with DNPH solution using a polarometric end-point. The results of the individual determinations were, however, subject to large errors, and the smooth course of titration was disturbed by current variations, which the authors think are due to fine particles of the 2,4-dinitrophenylhydrazones influencing the mercury dropping electrode. To eliminate interfering effects these authors used an ultrasonic system in their later work[6]. In the present paper we explain the causes of the unfavourable course of polarometric titrations encountered previously and we describe the conditions under which the direct polarometric titration of aromatic aldehydes by DNPH solution is successful.

## EXPERIMENTAL PART

### *Reagents*

A 0.01 *M* 2,4-dinitrophenylhydrazine solution (A.R. grade, Lachema) was prepared by dissolving 1.98 g of the substance in 1 l of 2 *N* hydrochloric acid. After two days the undissolved residue was filtered off and the factor was determined by titration with chloramine-T in the presence of potassium bromide[7].

96% Ethanol free of carbonyls was obtained by distillation from a mixture of 10 parts of pure ethanol and 1 part of 0.01 *M* DNPH solution in 2 *N* hydrochloric acid after boiling for 4 h.

Hydrochloric acid, thymol, gelatine (A.R. grade, Merck or Lachema), testosterone propionate (Spofa), and progesterone (Ciba) were used. Other investigated carbonyl compounds were of the highest available purity*, and their purity was checked gravimetrically[8] or by titration[3,9].

### *Apparatus*

Polarometric titrations were carried out with the conventional apparatus, using a mercury dropping electrode and a saturated calomel electrode with a cellophane diaphragm. The current was recorded by a microammeter having a range of 0 to 20 μA. Titrations were carried out in a conical vessel and oxygen was removed from the solution before as well as during the titration by bubbling with nitrogen. A 5-ml burette calibrated at 0.01 ml intervals was used.

Polarographic measurements were carried out on a type PO-4 Polariter instrument, manufactured by Radiometer, Denmark.

## RESULTS

For the fundamental experiments we chose vanillin, which is easily obtainable in a pure state and is readily soluble in water. Preliminary experiments showed that the reproducibility of the polarometric titration as well as the accuracy and precision of the determination were influenced by a number of factors, especially the potential used (EMF) and the sorption of the reagent on the precipitate.

### *(i) Influence of the potential used*

This was studied by the titration of 3 mg of vanillin in a volume of 15 ml of 2 *N* hydrochloric acid. In the polarometric titration the reduction of the aldehydic group cannot be used, as it follows the hydrogen wave. On the other hand in this medium the reduction of DNPH caused the appearance of a well developed polarographic

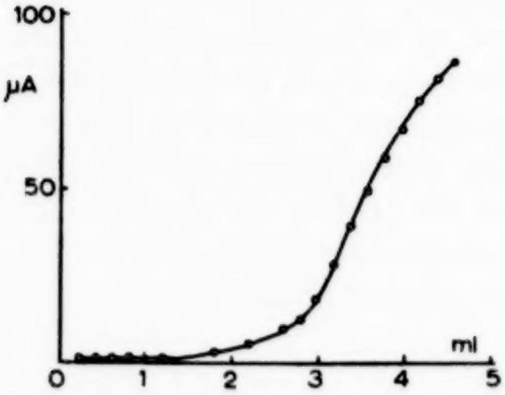

Fig. 1. Titration of 3.010 mg of vanillin in 15 ml 2 *N* HCl with 0.01 *M* DNPH solution in 2 *N* HCl.

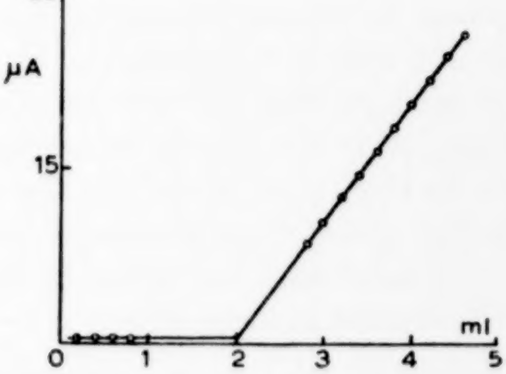

Fig. 2. Titration of 3.010 mg of vanillin in in 15 ml 2 *N* HCl with 0.01 *M* DNPH solution in 2 *N* HCl, in the presence of thymol.

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* We thank Mr. J. Dolník of the National Enterprise Aroma Prague, for letting us have a number of carbonyl compounds.

wave (*i.e.* from —0.3 V to —0.9 V *vs.* S.C.E.). When the titration was carried out at a potential of—0.7 V (*vs.* S.C.E.) large current variations were observed. Polarographic investigation showed that the precipitate of vanillin 2,4-dinitrophenylhydrazone formed was reduced on the mercury drop electrode at potentials of —0.65 V to —1.0 V (*vs.* S.C.E.). Thus it was possible to explain the current variations in titrations with a potential in this range. In further titrations we therefore used a potential of —0.4 to —0.6 V (*vs.* S.C.E.). Under these conditions it was possible to record reliably the value of the limiting current, but this value did not increase, after reaching the point of equivalence, linearly with increasing DNPH concentration — the straight line became curved (Fig. 1).

### *(ii) Investigation of the sorption of the reagent*

That the curvature of the course of the limiting current may be ascribed to sorption of DNPH on the precipitate was proved by a simple experiment:

*A.* To 15 ml of 2 *N* hydrochloric acid a 0.01-*M* DNPH solution in this 2 *N* acid was added in 0.2-ml portions. Current values were recorded each time after 3 min of bubbling nitrogen through the solution. With increasing reagent concentration the current increased linearly.

*B.* When this experiment was carried out under the same conditions in the presence of a precipitate corresponding to 3 mg of vanillin the current did not increase linearly, just as in the titration proper.

Indirect proof of the sorption was provided by the fact that addition of some surfactants or a change in the medium eliminated the curvature of the line. When the titration was carried out in the presence of gelatine (0.01%–0.05%) then the current increased linearly with increasing reagent concentration. The obtained results, however, possessed a large negative error (Table I), which we have not been able to explain.

TABLE I

INFLUENCE OF GELATINE CONCENTRATION ON THE TITRATION OF VANILLIN

3.051 mg of vanillin titrated with a 0.01-*M* DNPH solution in 2 *N* HCl; potential —0.5 V *vs.* S.C.E. Initial volume 15 ml 2 *N* HCl

| *Gelatine concentration at the beginning of the titration* % | *Vanillin found* mg | *Deviation* % |
|---|---|---|
| 0.050 | 2.932 | —3.9 |
| 0.030 | 2.919 | —4.4 |
| 0.015 | 3.005 | —1.5 |
| 0.010 | 2.902 | —4.9 |

Very good and reproducible results were obtained on adding thymol to the titrated solution in a minimum concentration of 0.002% provided that a potential of —0.4 V to —0.6 V (*vs.* S.C.E.) was used. At more negative potentials difficulties were again found owing to reduction of the precipitate. These difficulties could be eliminated by increasing the thymol concentration (0.02%).

In studying the influence of the ethanol concentration on the titration it was found that when its concentration was about 20% neither sorption of the reagent nor reduction of the precipitate (in a potential range of −0.4 V to −0.9 V *vs.* S.C.E.) occurred.

These results were proved by polarographic investigation.

### *(iii) Influence of the conditions of the titration*

Since reactions of carbonyl compounds with DNPH take place rapidly in acid medium, and since the reagent itself is very stable in 2 *N* hydrochloric acid, we first studied the influence of the acid concentration on the rate and stoichiometry of the titration of vanillin. The initial concentration in the titrated solution was 0 to 5 *N* hydrochloric acid, and the thymol concentration was always 0.02%. Throughout the concentration range the titration was quantitative (Table II). In a medium of 0.5 to 3 *N* hydrochloric acid it was possible to record current values after 3 min bubbling with nitrogen, whereas above or below this range it was necessary to wait for 7 to 10 min (especially at the beginning of the titration).

TABLE II

INFLUENCE OF THE CONCENTRATION OF HYDROCHLORIC ACID ON THE TITRATION OF VANILLIN

3.159 mg of the substance titrated with 0.01 *M* DNPH solution in 2 *N* HCl; potential −0.5 V *vs.* S.C.E., thymol concentration 0.02%

| *Initial HCl concentration N* | *Vanillin found (mg)* | *Deviation %* | *Note* |
|---|---|---|---|
| 0.00 | 3.044 | −3.7 | slow stabilisation of the current at first |
| 0.25 | 3.108 | −1.7 | |
| 0.50 | 3.219 | +1.8 | |
| 1.00 | 3.124 | −1.2 | |
| 2.00 | 3.170 | +0.3 | |
| 3.00 | 3.170 | +0.3 | |
| 4.00 | 3.091 | −2.2 | slow stabilisation of the current at first |
| 5.00 | 3.140 | −0.7 | |

TABLE III

INFLUENCE OF ETHANOL CONCENTRATION ON THE TITRATION OF VANILLIN

3.063 mg of vanillin titrated with 0.01 *M* DNPH solution in 2 *N* HCl, potential −0.5 V *vs.* S.C.E., initial volume 15 ml 2 *N* HCl

| *Initial ethanol concentration %* | *Vanillin found mg* | *Deviation %* |
|---|---|---|
| 60 | 3.035 | −0.9 |
| 40 | 3.018 | −1.4 |
| 30 | 3.048 | −0.5 |
| 20 | 3.032 | −1.0 |
| 15 | 2.989 | −2.4 |
| 10 | 2.959 | −3.4 |

Because most carbonyl compounds are insoluble in water the influence of ethanol on the course of the titration of vanillin was further studied. It was concluded (see

Table III) that at an initial concentration of 20 to 60% ethanol (the titrated solution did not contain thymol nor gelatine) the titration was rapid and quantitative. The current value could be recorded after only 3 min agitation of the solution. If the initial ethanol concentration was less than 20%, results were erratic because of sorption of the reagent on the precipitate. The quantitative course of the titration was proved by titration of 1 to 5 mg of vanillin in 15 ml of solution.

Three modifications of the procedure for the determination of aromatic aldehydes have been worked out, the choice of which depends partly on the solubility of the aldehyde and partly on the solubility in ethanol of the 2,4-dinitrophenylhydrazone formed.

## PROCEDURE

(*A*) To an amount of the substance corresponding to about 1 to 3 ml of 0.01 *M* aqueous solution of the aldehyde 2.5 ml of concentrated hydrochloric acid and 6 to 7 ml of 0.05% aqueous thymol solution are added. The solution is diluted to 15 ml with distilled water, nitrogen is bubbled through for 5 min and the solution is then titrated with a 0.01-*M* DNPH solution in 2 *N* hydrochloric acid. After each addition of the reagent (0.2 ml) the solution and the precipitate formed are agitated for about 3 min by bubbling nitrogen (until stabilisation of the current value). The titration is carried out at a potential of −0.4 V to −0.8 V (*vs.* S.C.E.). The recorded current values are corrected for the volume of the titrated solution.

(*B*) An amount of the substance corresponding to 1 to 3 ml of 0.01 *M* solution is dissolved in at least 5 ml of ethanol, 2.5 ml of concentrated hydrochloric acid are added, the solution is diluted to 15 ml and the procedure is continued as described under *A*.

(*C*) An amount corresponding to 1 to 3 ml of 0.01 *M* solution is dissolved in the least possible amount of ethanol, 6 to 7 ml of 0.05% thymol solution and 2.5 ml of concentrated hydrochloric acid are added, the solution is diluted to 15 ml and the procedure is continued as described under *A*.

Fig. 2 shows an example of the graph of the titration of vanillin according to procedure *A*.

## DISCUSSION OF RESULTS

From the results mentioned above, the main problem in the polarometric determination of carbonyl groups obviously consists of the "irregularities" appearing in the diffusion current of the titrant — DNPH. Another question is the non-linear increase in the current in titrations carried out in a medium of 2 *N* hydrochloric acid.

The polarographic investigation showed that in titrating with an incorrectly chosen potential, the diffusion current not only of the titrant, but also of the 2,4-dinitrophenylhydrazone precipitate formed, may exert an influence. The potential at which the reduction of the precipitate on the mercury drop electrode makes itself felt is influenced not only by the kind of substance which is subjected to condensation, but also by the composition of the solution in which the reaction takes place; this has been observed in similar cases[10]. The reduction current of the suspension is far higher when the suspension is agitated, *e.g.* by electromagnetic stirring, than when the suspension is motionless, when the reduction is conditioned by chance impacts of the particles on the electrode. In our case the precipitate settles rather slowly, so that its reduction would stop a long time after the suspension had ceased to move. A comparison of the half-wave potentials of DNPH and vanillin with the potential of the maximum of the corresponding hydrazone shows that in the reduction of the suspension the nitro groups are reduced. The so-called variation of the current observed by ZOBOV AND LIALIKOV[4-6] is thus explained. A polarographic investigation of the most suitable potential is therefore one of the conditions for obtaining quantitative results in further studies of these condensation reactions.

A second but no less important factor in the correct course of the titration is an elimination of the irregular increase in the current after the equivalence point has been reached. From a number of direct and indirect experiments, it seems that this effect may be explained by sorption of the titrant on the precipitate of the 2,4-dinitrophenylhydrazone, owing to intersurface forces, given by the character and composition of the phases touching each other. This sorption may be eliminated by the addition of gelatine (lower results), thymol or ethanol to the sample solution. These substances in sufficient concentration also eliminate the reduction of the 2,4-dinitrophenylhydrazone precipitate on the mercury dropping electrode.

The proposed polarometric determination of carbonyl groups will not, of course, be as universally applicable as the indirect methods in which a small excess of the reagent may be used, possibly at higher temperatures. The rapidity of the reaction, which is a condition of the direct titration, is influenced not only by the structure of the substance itself[2,9,11] but also by the medium in which the reaction occurs. From the

TABLE IV

REVIEW OF COMPOUNDS DETERMINED

| *Compound*[a] | *Amounts determined* | *Standard deviation, calculated from 10 determinations %* | *Procedure* |
|---|---|---|---|
| vanillin | 1.532–4.667 | 0.85 | A |
| (1.521) | 1.532–4.667 | 0.89 | B |
| | 1.532–4.667 | 0.61 | C |
| benzaldehyde (1.061) | 1.103–3.161 | 0.84 | |
| 3-ethoxy-4-hydroxybenzaldehyde (1.661) | 1.743–4.722 | 0.50 | A |
| *o*-nitrobenzaldehyde (1.511) | 1.487–4.512 | 0.75 | B[b] |
| *p*-nitrobenzaldehyde (1.511) | 1.509–4.571 | 0.66 | B[b] |
| cuminealdehyde (1.482) | 1.533–4.375 | 1.08 | B |
| piperonal (1.501) | 1.482–4.522 | 1.45 | B |
| protocatechuic aldehyde (1.381) | 1.352–4.115 | 0.91 | C |
| cinnamic aldehyde (1.321) | 1.277–4.089 | 0.70 | B[b] |
| salicylaldehyde (1.221) | 1.270–3.582 | 0.86 | B |

[a] Figures in brackets denote how many mg of the compound correspond to 1 ml 0.01 *M* DNPH.

[b] Under the conditions specified the compound to be determined is also polarographically reduced and thus the V-shaped curve of the titration is obtained (reduction of nitro-group or double bond respectively).

results it is clear that a 2-*N* hydrochloric acid medium is well suited to the direct titration, particularly since the titrant is stable in this solution. Therefore substances soluble in water are best determined according to procedure *A*.

Ethanol must be used to dissolve certain compounds, but the hydrazones formed may then be partly soluble, which unfavourably influences the course of the titration. In such a case the substance is dissolved in the least possible amount of ethanol, and the determination is carried out according to procedure *C*. If the concentration of ethanol necessary to hold the substance in solution is sufficient to prevent sorption of the reagent on the precipitate, the analysis is carried out according to procedure *B*. Examples of determinations of aromatic aldehydes according to the different procedures are given in Table IV.

As can be seen from this table, the proposed method is particularly suitable for the determination of aromatic aldehydes which react easily with DNPH. The reactivity of aromatic aldehydes is of course influenced by the substituents on the aromatic ring, so that the method is not universal even for aromatic compounds. For instance we have not succeeded in determining *p*-aminobenzaldehyde.

In experiments on the determination of ketones ($\omega$-chloroacetophenone, benzoin, testosterone, testosterone propionate, progesterone) and aliphatic aldehydes (7-hydroxycitronellal, citral, undecylaldehyde, formaldehyde and acetaldehyde) we have not obtained satisfactory results, partly because of the low reaction rate, and partly owing to the large solubility of the 2,4-dinitrophenylhydrazones formed.

## ACKNOWLEDGEMENT

We thank K. MICKA, C.Sc. of the Polarographic Institute of the Czechoslovak Academy of Sciences for the polarographic investigation of the reduction of the hydrazone.

## SUMMARY

In the polarometric titration of aromatic aldehydes with a 2,4-dinitrophenylhydrazine solution, the sorption of the reagent on the hydrazone precipitate and the reduction of this precipitate at the mercury dropping electrode have been proved. These effects may be eliminated by the addition of thymol or ethanol to the sample solution, so that most aromatic aldehydes can be determined.

## RÉSUMÉ

Une méthode est proposée pour le titrage polarométrique des aldéhydes aromatiques, au moyen de dinitro-2,4-phénylhydrazine.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von aromatischen Aldehyden durch polarometrische Titration mit 2,4-Dinitrophenylhydrazinlösung.

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# RAPID DETERMINATION OF ALUMINIUM IN BERYLLIUM METAL BY CATHODE RAY POLAROGRAPHY

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(Received February 21st, 1961)

## INTRODUCTION

Despite the rapidly increasing use of beryllium in the atomic energy field, no completely satisfactory procedure has been published for the determination of aluminium in beryllium metal although it is one of the impurities most frequently analysed for. The principal methods in use appear to be the 8-hydroxyquinoline gravimetric procedure[1,2], a spectrographic procedure[3], and a polarographic procedure using Solochrome Violet RS (5-sulpho-2-hydroxybenzene-azo-2-naphthol)[4]. The gravimetric method suffers from the disadvantage of requiring an inconveniently large sample, whilst the polarographic method as described by PERKINS AND REYNOLDS[4] is too lengthy for routine use. PERKINS AND REYNOLDS found that beryllium tended to precipitate at the pH normally used for the determination of aluminium with Solochrome Violet RS, but even when precipitation was avoided, a considerable depression of the aluminium-dye reduction step occurred. To overcome this effect these workers carried out a preliminary separation of aluminium from the bulk of the beryllium by a 8-hydroxyquinoline extraction.

The dye Superchrome Garnet Y (5-sulpho-2',4',2-trihydroxyazobenzene, C.I. 168) is known to react with aluminium at a lower pH than Solochrome Violet RS[5], and when used in conjunction with a highly sensitive cathode ray polarograph, the depressing effect of beryllium is minimized and the necessity of separating aluminium is obviated. A direct method is described for the determination of aluminium in beryllium metal after a rapid mercury cathode electrolysis to remove iron and other impurities. The sample weight required is only 100 mg, and a single determination may be completed in little over an hour.

### *The reaction of aluminium with Superchrome Garnet Y in the presence of beryllium*

Superchrome Garnet Y, at concentrations below $2 \cdot 10^{-5}$ *M*, exhibits sharp, well-defined "adsorption-reduction" peaks on the cathode ray polarograph[6] (Fig. 1). In the presence of aluminium in acetate buffers, the dye peak is reduced in height, and a new peak appears at a more negative potential, its height being proportional to the aluminium concentration (Fig. 2). At pH 3.40 the sensitivity is 6.33 $\mu$A/$\mu$g Al/ml. Although beryllium does not produce a discrete reduction peak, relatively high concentrations cause a depression of the aluminium-dye peak (Fig. 3). However, it was found that at a constant beryllium concentration and a favourable pH, a linear relationship was still obtained between peak height and aluminium concentration. A pH range of 3.4–3.5 is optimum for the determination, since the sensitivity decreases rapidly at lower pH values, whilst at higher values the peak height is not proportional to the aluminium concentration.

It may be seen from Fig. 3 that for an error of less than 2% in the aluminium determination the sample weight of beryllium metal should be controlled so that the final beryllium concentration is within ± 3% of that used in the calibration curve. If a sample weight outside this range is inadvertently taken, an approximate result may be obtained by reference to a depression factor (ratio of peak height in the presence of beryllium to peak height in the absence of beryllium) curve such as Fig. 3.

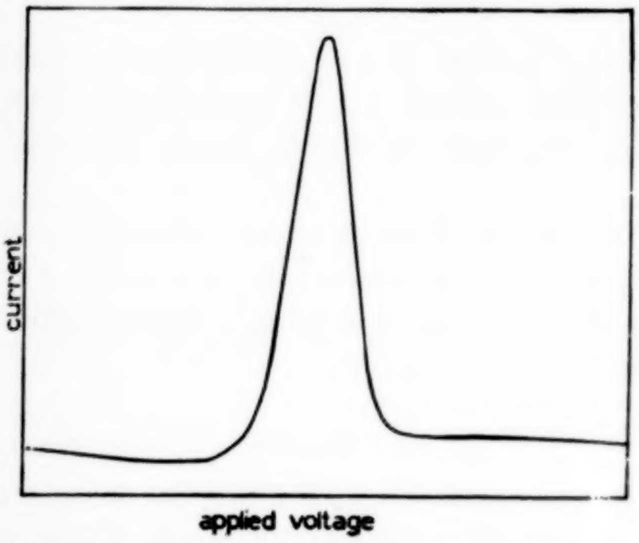

Fig. 1. Oscillogram of Superchrome Garnet Y in an acetate buffer of pH 3.40. Dye concentration $= 1 \cdot 10^{-5}$ *M*; peak height = 5.1 μA; peak potential = —0.30 V *vs*. Hg pool.

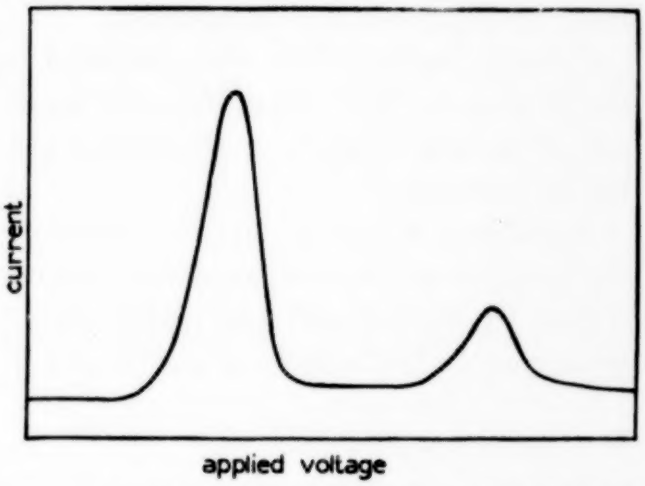

Fig. 2. Oscillogram of Superchrome Garnet Y, plus aluminium in an acetate buffer of pH 3.40. Dye concentration $= 1 \cdot 10^{-5}$ *M*; aluminium concentration $= 6 \cdot 10^{-6}$ *M*; 1st peak height = 3.8 μA, 1st peak potential = —0.30 V *vs*. Hg pool; 2nd peak height = 1.0 μA, 2nd peak potential = —0.51 V *vs*. Hg pool.

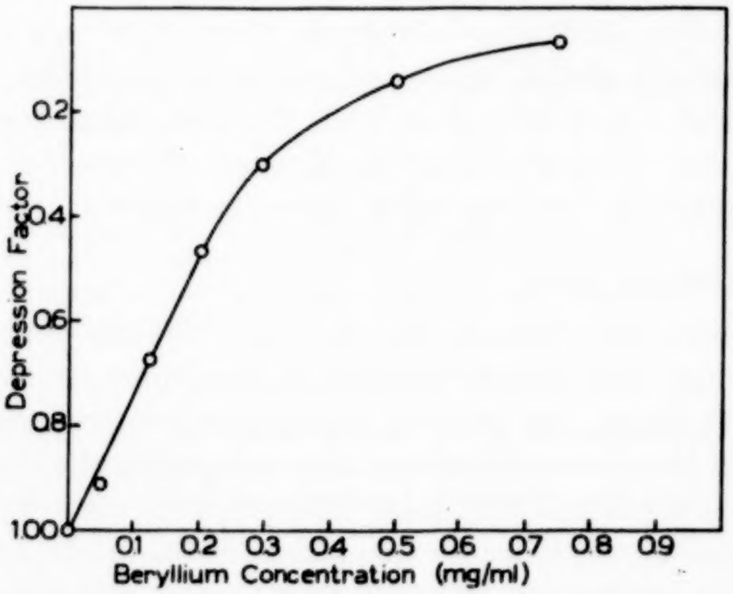

Fig. 3. Depression by beryllium of the aluminium–dye reduction peak.

## EXPERIMENTAL

### *Apparatus*

Polarograph: The linear-sweep cathode ray polarograph was supplied by Southern Instruments Computer Division, Surrey, England. This instrument has a sweep rate of 0.25 V/sec and a delay period of 5 sec. The dropping mercury capillary characteristics were $m = 1.14$ mg/sec, $t = 6.5$ sec (—0.5 V *vs.* pool). All measurements were made in a thermostated bath at 25.0 ± 0.2°.

Mercury cathode cell: The small "constant-current" mercury cathode cell has been described previously[7].

### *Reagents*

Superchrome Garnet Y: The crude dye was prepared as described by COONEY AND SAYLOR[5], then purified by a double recrystallization from water. The purity of the final product was not determined.

Acetate buffer: This was prepared by mixing 500 ml of 1 *M* ammonium acetate (from reagent grade ammonia and acetic acid) with 470 ml of 1 *M* hydrochloric acid, and adjusting to pH 3.40 ±0.05 on a pH meter. The buffer should be stored in a polythene container.

Beryllium metal standard: "Spec-pure" beryllium from Johnson, Matthey and Co. Ltd., London, was used for calibration purposes, and was found to contain 120 p.p.m. of aluminium. The water used throughout was demineralised, then distilled from quartz and collected and stored in a polythene container.

### *Recommended procedure*

Weigh accurately 100 ± 3 mg of fine beryllium metal filings. Dissolve by warming with 16 ± 1 ml of 1 *N* sulphuric acid. Dilute to 25 ml in a volumetric flask. Transfer about 10 ml of the sample solution to the dry mercury cathode cell and electrolyse at 9 V (0.5 A) for 15–20 min. Remove the air condenser and, with current still flowing, withdraw about 5 ml of the solution. Cool to room temperature, take a 2-ml aliquot and neutralize to pH 3–4 with 1 *N* ammonium hydroxide, using indicator paper. Transfer to a 25-ml volumetric flask, add 5 ml of acetate buffer (pH 3.40), 5 ml of a $5 \cdot 10^{-5}$ *M* dye solution, and dilute to volume. Heat at 70° in a water bath for 10–15 min, cool, and transfer a portion to the polarographic cell. After deaeration, measure the peak height of the wave at —0.51 V *vs.* Hg pool, using a starting potential of —0.32 V. A blank must be carefully carried through the procedure, and the measured peak height multiplied by the depression factor to obtain a true blank peak height.

### *Construction of calibration curve*

A calibration curve was obtained by "spiking" 100-mg portions of "spec-pure" beryllium metal filings with known amounts of aluminium, and carrying through the procedure described above, but omitting the mercury cathode electrolysis step. The relevant depression factor was determined by comparing the slope of this line with that obtained in the absence of beryllium. The minimum concentration of aluminium measurable is governed mainly by the magnitude of the blank, and, using the recommended procedure, is equivalent to about 20 p.p.m. of aluminium in beryllium.

### *Study of interferences*

The concentration of aluminium in nuclear-grade beryllium metal is usually in the range 100–2,000 p.p.m. Other impurities commonly found are[1] Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn. With the exception of iron, these impurities are normally present at a lower concentration than aluminium, but even small amounts of nickel, lead and molybdenum interfere with the direct determination of aluminium using Superchrome Garnet Y. A mercury cathode electrolysis employing the cell described was found to rapidly remove all interfering elements from a 0.2 *N* sulphuric acid electrolyte.

TABLE I

RECOVERY OF ALUMINIUM FROM BERYLLIUM USING SUGGESTED PROCEDURE

| *Al added (μg)* | *Al found (μg)* | *% recovery* |
|---|---|---|
| nil | 12 | — |
| 10 | 20 | 91 |
| 20 | 31 | 97 |
| 50 | 59 | 94 |
| 75 | 85 | 97 |
| 100 | 117 | 105 |
| 150 | 162 | 100 |
| 200 | 208 | 98 |

Each solution contained 0.100 ± 0.001 g of "spec-pure" beryllium metal, plus 500 μg of each of the following elements: Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn.

### *Analysis of synthetic samples*

A series of solutions containing 100 mg of "spec-pure" beryllium metal was "spiked" with known amounts of aluminium, and 500 μg of each of the 14 impurities mentioned above. These solutions were then analysed for aluminium by the recommended procedure; the results are tabulated in Table I.

## SUMMARY

A rapid method is presented for the determination of aluminium in beryllium metal by cathode ray polarography using the dye Superchrome Garnet Y. A mercury cathode electrolysis is used to remove heavy metal impurities, but the need for a separation of aluminium from beryllium is avoided. A single determination requiring a 100-mg sample may be completed in little over an hour, with normal polarographic precision.

## RÉSUMÉ

Une méthode rapide est proposée pour le dosage de l'aluminium dans le béryllium, par polarographie à rayons cathodiques, au moyen du colorant "Superchrome Garnet Y". Le fer et d'autres impuretés doivent être éliminés au préalable par électrolyse sur cathode de mercure. La séparation aluminium-béryllium peut être évitée.

## ZUSAMMENFASSUNG

Beschreibung einer raschen Methode zur Bestimmung von Aluminium in Beryllium durch Kathodenstrahlenpolarographie unter Verwendung des Farbstoffes Superchrom Garnet Y. Störende Schwermetalle werden durch Elektrolyse mit einer Quecksilberkathode entfernt. Eine Trennung des Aluminiums von Beryllium ist nicht notwendig.

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# EINFACHES DESTILLATIONSVERFAHREN ZUR TITRIMETRISCHEN BESTIMMUNG VON KOHLENDIOXYD

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(Eingegangen den 31. Januar, 1961)

Die beiden grundlegenden Probleme der Kohlendioxydbestimmung bestehen in der Isolierung und Messung des Kohlendioxyds. Vor kurzem beschäftigten sich BELCHER, THOMSON UND WEST[1] eingehend mit dieser Frage. Genannte Autoren fingen das bei der Verbrennung organischer Stoffe entstehende Kohlendioxyd in Bariumhydroxydlösung auf und titrierten den Überschuss des Bariumhydroxyds mit Säure zurück. Die Ergebnisse ihrer Versuche lassen sich kurz wie folgt zusammenfassen: Die Absorption des Kohlendioxyds ist ein langsamer Prozess und das kohlendioxydhaltige Gasgemisch muss in Form sehr kleiner Bläschen und in langsamem Strom durch die absorbierende Flüssigkeit geleitet werden. Die quantitative Überführung des Inhalts des Absorptionsgefässes in den Titrierkolben bedeutet dabei ein besonderes Problem. Den auf die Aufnahme der Luftkohlensäure zurückführbaren Fehler schalten die genannten Autoren mit unter identischen Verhältnissen durchgeführten blinden Proben aus.

Mit dem Problem der Titration beschäftigten sich mehrere Forscher, die zitierte Mitteilung gibt einen guten Überblick über die erreichten Ergebnisse. Um die bei der Rücktitration des Bariumhydroxydüberschusses durch Adsorption entstandenen Fehler auszuschalten, wird vorgeschlagen, die Messlösung in kleinen Portionen zuzugeben.

SCHULEK *et al.*[2] saugten das Kohlendioxyd in einen Bariumhydroxydlösung enthaltenden evakuierten Kolben. Der Überschuss des Bariumhydroxyds wurde dann nach mehrmaligem Umschütteln und entsprechender Wartezeit unter Anwendung von Pentan als Sperrflüssigkeit zurücktitriert. Mit diesem Verfahren konnte einesteils der auf die unvollständige Absorption des Kohlendioxyds zurückführbare Fehler und anderenteils die Umspülung der zu titrierenden Flüssigkeit und die störende Wirkung der Luftkohlensäure ausgeschaltet werden. Das Verfahren erwies sich als geeignet zur Bestimmung des Kohlendioxydgehalts von Karbonaten und des bei der Verbrennung organischer Stoffe gebildeten Kohlendioxyds.

Zur Isolierung des bei verschiedenen Reaktionen gebildeten Kohlendioxyds schien uns die Anwendung des Destillationsprinzips vorteilhaft zu sein. Offen stand dabei lediglich die Frage, unter welchen Bedingungen die vollkommene Absorption des Kohlendioxyds in der als Vorlage verwendeten Bariumhydroxydlösung unter gleichzeitiger Fernhaltung des eventuell vorhandenen Kohlendioxydgehalts der Atmosphäre gewährleistet ist.

Zwecks Ausschaltung der störenden Wirkung der Luftkohlensäure wird die Bariumhydroxydlösung mit Pentan überschichtet. Unter solchen Bedingungen ist die störende Wirkung auf ein Mindestmass herabgesetzt. Das Pentan bedeckt die Lösungsoberfläche nicht nur als Flüssigkeit, sondern verdampft infolge seiner Flüchtigkeit auch teilweise, füllt nach Ausdrücken der Luft mit den Dämpfen den gesamten Luftraum des Kolbens vollständig aus und hält die Luftkohlensäure auf diese Weise auch von der an der Kolbenwand haftenden Bariumhydroxydlösung fern. Absorption und Titration erfolgen in demselben Gefäss, ein Umstand, der hinsichtlich der Genauigkeit der Messung einen besonderen Vorteil bedeutet.

Die Durchführung der Destillation weicht von den allgemein bekannten Methoden darin ab, dass bei diesem Verfahren keine Bläschen durch die absorbierende Lösung passieren können. Diese Einschränkung muss streng befolgt werden, damit mit den aus der Lösung austretenden Gasbläschen auch keine Kohlensäure verloren geht. Dieses Prinzip wurde durch WINKLER[3] bei der Trennung geringer Bromidmengen durch destillieren in Form von elementarem Brom sowie durch SCHULEK UND VASTAGH[4] zur Destillation des Ammoniaks verwendet.

Diese beschriebenen Verfahren mussten zur Bestimmung der Kohlensäure durch Auskochen derart verfeinert werden, dass die vollkommene Absorption der Kohlensäure gesichert werden konnte. Dies ist durch Einführung bzw. Ausarbeiten des Prinzips der stufenweisen Abkühlung der Dämpfe erreicht worden.

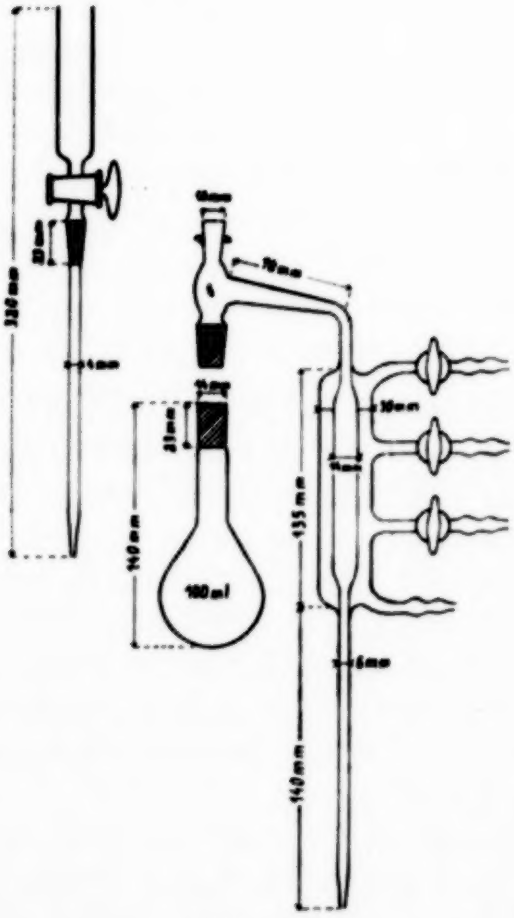

Fig. 1.

Zu diesem Behufe wurde der SCHULEK'sche Destillationsapparat (Fig. 1) an seinem Kühlerteil etwas abgeändert. Der Kühlmantel besitzt anstatt 2, 4 Ein- bzw. Ausflussröhrchen, aus welchen die drei oberen mit Glashahn versehen sind. Das untere Röhrchen wird als Einfluss-, die drei oberen abwechselnd als Ausflussrörchen benutzt, wodurch der Kühler bzw. die durchströmenden Dämpfe in drei Stufen abgekühlt werden können. Somit ist aber auch die bequeme Destillation bzw. Absorption der Dämpfe und Gase ohne durchströmenden Gasbläschen gesichert.

Man arbeitet nun wie folgt. Zuerst wird die Apparatur durch lebhaftes Kochen des entsprechend vorbereiteten Reaktionsgemisches aber ohne Kühlung luftleer gemacht. Nun wird die Absorptionsflüssigkeit als Vorlage — nachdem die erste Stufe der Kühlung eingestellt worden ist — unter weiter genau angegebenen Versuchsbedingungen vorgeschaltet. Der Vorlagekolben wird dem Kühlerrohr sanft angedrückt und die zweite Stufe der Kühlung in Gang gesetzt. Die Absorptionsflüssigkeit steigt nun in dem Kühlerrohr. Die Höhe des Aufsteigens kann durch Schliessen des zweiten bzw. durch Öffnen des dritten Abflussröhrchens eingestellt bzw. geändert werden. Lässt man nun durch das eingeschliffene Trichterröhren das geeignete Reagens oder die Untersuchungslösung behutsam in den Destillierkolben einfliessen, so kann das freigemachte Kohlendioxyd bequem abdestilliert und die Absorption desselben durch die Bariumhydroxyd-Lösung „ohne Gasbläschen" durchgeführt werden. Genaue Vorschrift wird in dem Abschnitt BESCHREIBUNG DES VERFAHRENS angegeben.

Während der Destillation muss für gleichmässiges Sieden Sorge getragen werden. Dies lässt sich mit entsprechend vorbereitetem und zerkleinertem Bimsstein (Korngrösse 1.5–2 mm), sowie mit adäquater Regelung der Heizung erreichen. Der Kolben wird mit einem kleinen elektrischen Heizkörper erwärmt, dessen Leistung mit Hilfe eines Schiebewiderstandes geregelt werden kann. Der Heizkörper (siehe Fig. 2) ist eine auf Isoliermaterial niedriger Wärmekapazität befestigte Heizspirale, die in direktem Kontakt mit dem Destillierkolben steht. Eine wesentliche Vorbedingung bei der Konstruktion des Heizkörpers ist, dass die Aufheizung bzw. Abkühlung des Kolbens mit der Veränderung der Stromstärke rasch erfolgt. Die Menge des im Laufe der Destillation übergehenden Kohlendioxyds lässt sich mit der Intensität des Siedens regeln, so muss nötigenfalls durch entsprechende Einstellung des Schiebewiderstandes dafür gesorgt werden, dass das plötzlich freiwerdende Kohlendioxyd nicht in Form von Blasen in den Vorlagekolben gelangt.

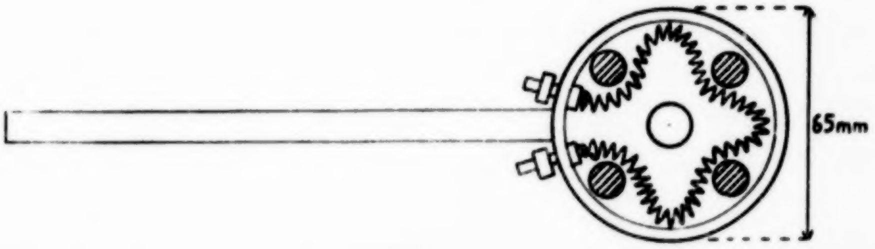

Fig. 2.

Zur Sicherung einer „blasenfreien" Destillation stehen uns also zwei Möglichkeiten zur Verfügung: einerseits die in drei Abstufungen regelbare Wasserkühlung, andererseits die Heizung. Die Regelung der Heizung ist bei richtig geführter Destillation praktisch nicht notwendig. Nach Einsetzen des Siedens lässt sich die Destillation bei gleichmässiger Heizung durchführen; lediglich für eine entsprechende Regelung der Kühlung muss gesorgt werden. Man stellt die Strömungsgeschwindigkeit des Kühlwassers während der Destillation so ein, dass das Wasserniveau im Kühlmantel beim Übergang auf eine mässigere Kühlungsintensität leicht absinkt. Zu diesem Zwecke soll das Ende des an den oberen Ausflussstutzen angeschlossenen Gummischlauches bezogen auf die beiden unteren relativ hoch stehen, damit das Wasser dann frei zurückströmen kann.

Die beschriebene Destillationsmethode ist zur Bestimmung des Kohlendioxydgehalts wasserlöslicher und in Wasser schwer löslicher Karbonate, sowie Kohlendioxyd-haltiger Lösungen und des bei der Oxydation oder Zersetzung organischer Stoffe gebildeten Kohlendioxyds geeignet. Bei der Bestimmung des Kohlendioxydgehalts schwer löslicher Karbonate wird die mit Bariumhydroxyd alkalisch gemachte wässrige Suspension des Karbonats im Destillierkolben untergebracht, das System mit dieser entlüftet und die zum Freimachen des Kohlendioxyds notwendige Säure durch den Hahntrichter zugegeben. Zur Messung des bei Oxydationsprozessen gebildeten Kohlendioxyds wird das System in der Regel durch Kochen der wässrigen Lösung des Oxydationsmittels entlüftet und die Lösung des zu oxydierenden Stoffes dann durch den Hahntrichter zugegeben.

Wir führten mit der oben umrissenen Methode Messungen im 0.1 und 0.01 $N$ Massstabe durch und fanden dabei, dass das Verfahren die bequeme und genaue Bestimmung von 22–0.22 mg $CO_2$ ermöglicht. Ein grosser Vorteil der Methode besteht darin, dass bei der Bestimmung von 20–2 mg $CO_2$ im 0.1 $N$ Massstabe keine „blinde" Destillation durchgeführt werden muss. Die störende Wirkung der Luftkohlensäure ist unter solchen Bedingungen nicht grösser als der Tropfenfehler. Zur Bestimmung geringerer Kohlendioxydmengen wird 0.01 $N$ Bariumhydroxydlösung verwendet. Die Ergebnisse der „blinden" Destillation sind unter solchen Bedingungen beachtlich; während der Destillation und Titration gelangen 0.2–0.3 ml 0.01 $N$ Bariumhydroxyd entsprechende Kohlendioxydmengen in das System.

Bei der Titration des Kohlendioxyds im 0.01 $N$ Massstabe werden die Ergebnisse auch durch das Volumen der Lösung beeinflusst, es soll daher sorgfältig darauf geachtet werden, dass die Lösungsvolumina zu Beginn der Titration gleich gross sind. Wir führten unsere Messungen mit Lösungsvolumina von 50 ml durch. An den Titrationskolben wurde das Volumen von 50 ml bezeichnet und die Lösungen wurden nach der Destillation mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Nach einer entsprechenden Praxis beträgt die Genauigkeit der Bestimmung im 0.01 $N$ Massstabe $\pm$ 0.03 ml 0.01 $N$ Bariumhydroxydlösung, entsprechend $\pm$ 7 $\mu$g Kohlendioxyd.

Wir bestimmten mit dieser Methode zuerst den Kohlendioxydgehalt von Kaliumhydrokarbonatlösungen und Kalzitproben. Auf Grund der Ergebnisse dieser Messungen wurden die Bedingungen der Destillation und Titration sowie die Genauigkeit des Verfahrens festgestellt. Aus der Reihe der Oxydationsreaktionen führten wir die Oxydation des Oxalats mit Kaliumpermanganat durch und bestimmten die Menge des gebildeten Kohlendioxyds. Hierzu sei erwähnt, dass es uns gelang, die Bestimmung der sehr stabilen komplexen Oxalate [$K_3Co(C_2O_4)_3 \cdot 3.5\ H_2O$ und $K_3Cr(C_2O_4)_3 \cdot 3\ H_2O$] über die bei ihrer Oxydation gebildete Kohlensäure durchzuführen.

Wir bestimmten auch den Kohlendioxydgehalt der mit Kalciumoxyd karbonatfrei gemachten normalen Natriumhydroxydlösung sowie der 0.1 $N$ Bariumhydroxydlösung und der (50%-igen) Sörensenschen „karbonatfreien" Natronlauge. Bei diesen Bestimmungen wurden die Lösungen im Destillationskolben unter eine Pentanschicht eingebracht und die Entlüftung durchgeführt.

Zu den Spülungen sowie zur Ergänzung der Lösungsvolumina usw. verwendeten wir in jedem Falle frisch ausgekochtes destilliertes Wasser, das nach dem Abkühlen mit einer 0.5 cm dicken Pentan-Phase überschichtet wurde. Die Bariumhydroxydlösungen werden in den üblichen automatischen Büretten gelagert, jedoch auch in diesen noch zusätzlich mit Pentan überschichtet.

## BESCHREIBUNG DES VERFAHRENS

### *Reagenzien*

0.1 *N* Bariumhydroxydlösung (mit 5% Bariumchlorid); 0.01 *N* Bariumhydroxydlösung (mit 5% Bariumchlorid und 30% Äthanol); 0.1 bzw. 0.01 *N* Salzsäure; 20%-ige Schwefelsäure; 2%-ige Salzsäure; 0.3%-ige alkoholische Thymolblaulösung; 5%-ige Kaliumpermanganatlösung; Bimsstein (Körngrösse 1.5–2 mm); Pentan.

### *Bestimmung des Kohlendioxydgehalts wasserlöslicher Karbonate*

Aus der zu untersuchenden Substanz wird mit vorher ausgekochtem und abgekühltem destilliertem Wasser eine Stammlösung hergestellt. 10.00 ml dieser Lösung sollen bei der Bestimmung im 0.1 *N* Massstabe 10–20 mg, bei Bestimmung im 0.01 *N* Massstabe 1–2 mg Kohlendioxyd enthalten.

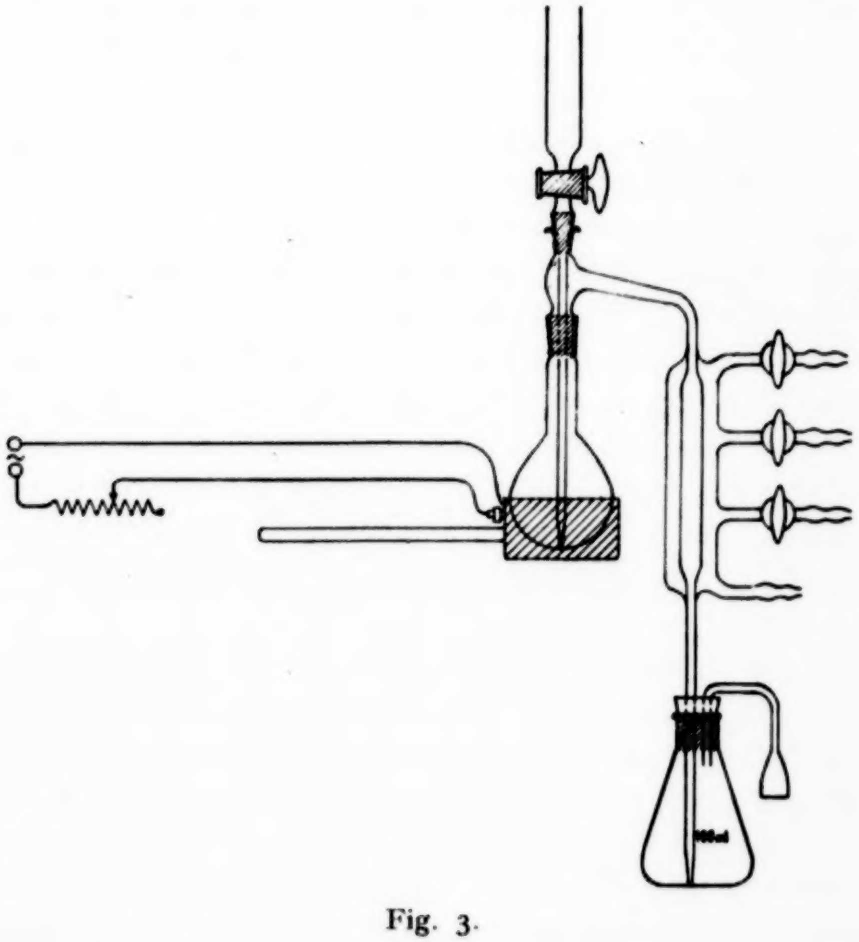

Fig. 3.

Das Einlaufrohr des Hahntrichters im Destillationskolben wird mit ausgekochtem destilliertem Wasser blasenfrei aufgefüllt. Zweckmässig saugt man das Wasser von unten in das Rohr und verschliesst dann den Hahn.

Der 100-ml Kolben des Destillationsapparats wird mit 5 ml Schwefelsäure beschickt und diese mit Wasser auf *ca.* 50 ml ergänzt. Man bringt nun einige Körner Bimsstein in den Kolben, stellt den Apparat zusammen und schaltet die Heizung ein. Nach

Einsetzen des Siedens wird der Schiebewiderstand so eingestellt, dass die Lösung lebhaft und gleichmässig siedet. Nachdem aus dem Ausflussrohr des Kühlers ein lebhafter Wasserdampfstrom entweicht, wird 1 Min gewartet, dann öffnet man den unteren Hahn am Kühler, verschliesst die beiden oberen und schaltet das Kühlwasser ein. In einen 100-ml fassenden Erlenmeyer-Schliffkolben werden 5 ml Pentan gegossen und dann aus einer automatischen Bürette 15.00 ml Bariumhydroxydlösung einlaufen gelassen. Bei der Bestimmung geringer $CO_2$-Mengen im 0.01 *N* Massstabe wird das Volumen von 50 ml am Kolben vorher bezeichnet. Man spült nun die Innenwand des Kolbens mit 5 ml ausgekochtem destilliertem Wasser nach, und befestigt den Kolben dann an dem am Ausflussrohr des Kühlers befindlichen, doppelt durchbohrten Korke (Fig. 3). Durch die eine Bohrung des Korkes geht dabei das Kühlerrohr, durch die andere wird über ein ungebogenes Glasrohr eine Trockenröhre angeschlossen, die mit Bariumhydroxydlösung angefeuchtete Watte enthält. Der Korkstopfen kann am Kühlerrohr auf- und abgeschoben und der Kolben so leicht gehoben oder gesenkt werden. Das Ende des Ausflussrohrs soll dabei locker am Boden des Kolbens aufliegen. Nun wird der mittlere Hahn am Kühler geöffnet und der untere verschlossen, worauf die Bariumhydroxydlösung im Kühlerrohr bis ungefähr ins untere Drittel ansteigt. Man pipettiert hierauf 10.00 ml der vorbereiteten Lösung in den Hahntrichter und lässt diese dann durch vorsichtiges Öffnen und Schliessen des Hahnes in kleineren Portionen (zu *ca.* 0.5 ml) in den Destillationskolben einlaufen. Unterdessen wird die Höhe der Bariumhydroxydlösung im Kühlerrohr beobachtet, und falls notwendig, wird die dritte Kühlungsstufe, durch Öffnen des obersten Hahnes und Schliessen des mittleren, eingeschaltet. Der Hahntrichter wird hierauf zuerst mit 10 und dann mit 5 ml ausgekochtem destilliertem Wasser nachgespült. Auch beim Spülen ist darauf zu achten, dass nur kleine Anteile des Wassers in den Kolben gelassen werden, da im entgegengesetzten Fall das Sieden aussetzen kann, und die Bariumhydroxydlösung aus der Vorlage in den Destillationskolben zurückgezogen wird. Nach der Spülung des Hahntrichters wird der Vorlagekolben vorsichtig um 1–2 mm gesenkt und dadurch der Austausch der Bariumhydroxydlösung zwischen dem Inneren des Kühlerrohres und dem Vorlagekolben infolge der Auf- und Abwärtsbewegung der Flüssigkeit beschleunigt. Die Destillation wird 15–20 Min hindurch fortgesetzt. Man öffnet nun den unteren Hahn des Kühlers, worauf die Bariumhydroxydlösung aus dem Kühlerrohr verdrängt wird. Der Vorlagekolben wird nun so weit gesenkt, dass das Ende des Kühlerrohres über die Flüssigkeitsoberfläche zu stehen kommt, setzt das Sieden noch 1 Min hindurch fort, wodurch das Innere des Kühlerrohres mit Wasser ausgespült wird und beendet dann das Sieden. Nach Abnahme des Vorlagekolbens (bei Messungen im 0.01 *N* Massstabe ist sein Inhalt mit ausgekochtem destilliertem Wasser(!) auf 50 ml zu verdünnen) wird die Vorlageflüssigkeit in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 bzw. 0.01 *N* Salzsäure bis zum Farbumschlag auf grün titriert. Während der langsam durchgeführten Titration soll die Flüssigkeit energisch gerührt werden. Sobald die blaue Farbe zu verblassen beginnt, wird die Lösung energisch durchgeschüttelt und diese Operation bis zum Erreichen des Endpunktes öfters wiederholt. Bei Bestimmungen im 0.01 *N* Massstabe wird mit ausgekochtem destilliertem Wasser, dessen Volumen dem Volumen der zu untersuchenden Lösung und der Spülflüssigkeit entspricht, eine blinde Probe durchgeführt. Der Unterschied zwischen den Ergebnissen der beiden Titrationen ist mit der Menge des Kohlendioxyds proportional. Im 0.1 *N* Massstabe ist die blinde Probe nicht notwendig, in diesem Falle werden die 15 ml der Bariumhydroxydlösung (in Gegenwart von 5 ml Pentan als Sperrflüssigkeit) mit 0.1 *N* Salzsäure titriert. 1 ml 0.1 *N* bzw. 0.01 *N* Salzsäure entspricht 2.2005 bzw. 0.22005 mg Kohlendioxyd.

Die Ergebnisse unserer Untersuchungen sind in Tabelle I zusammengefasst.

TABELLE I

BESTIMMUNG DES $CO_2$-GEHALTS IN $KHCO_3$-LÖSUNG

| *Einwaage $CO_2$ als $KHCO_3$-* Lösung, mg* | *Verbrauch 0.1 N Bariumhydroxydlösung, ml* | | *Gefunden $CO_2$* | |
|---|---|---|---|---|
| | *Einzeln* | *Durchschnitt* | *mg* | *Δ%* |
| 21.64 | 9.83<br>9.82 | 9.82 | 21.61 | —0.1 |
| 10.86 | 4.93<br>4.94 | 4.93 | 10.85 | —0.1 |
| 5.44 | 2.47<br>2.48 | 2.47 | 5.44 | 0.0 |
| | *Verbrauch 0.01 N Bariumhydroxydlösung, ml* | | | |
| | *Einzeln* | *Durchschnitt* | | |
| 2.067 | 9.37<br>9.39 | 9.38 | 2.064 | —0.1 |
| 1.025 | 4.65<br>4.63 | 4.64 | 1.021 | —0.4 |
| 0.411 | 1.86<br>1.85 | 1.86 | 0.409 | —0.4 |

* Der $CO_2$-Gehalt der $KHCO_3$-Lösung wurde durch Messung mit Bariumhydroxyd auch direkt kontrolliert.

### *Bestimmung des Kohlendioxydgehalts des Kalzits*

0.04–0.07 g grob zerkleinertes Kalzit (Islandischer Kalkspat) wird analytisch genau eingewogen und mit ausgekochtem destilliertem Wasser in den Destillationskolben gespült. Der Kolbeninhalt wird auf 30–50 ml ergänzt und mit 1 ml 0.1 *N* Bariumhydroxydlösung alkalisch gemacht. Nach Zugabe von Bimsstein wird der Apparat unverzüglich zusammengestellt und die Heizung eingeschaltet. Die Entlüftung und Einstellung des Vorlagekolbens führt man genau so durch wie im vorangehenden Abschnitt beschrieben wurde. Als Vorlageflüssigkeit werden 20.00 ml 0.1 *N* Bariumhydroxydlösung verwendet. Durch den Hahntrichter lässt man 10 ml 2%-ige Salz-

TABELLE II

BESTIMMUNG DES KALZITS ÜBER KOHLENDIOXYD

| *Einwaage Kalzit mg* | *Verbrauch 0.1 N Bariumhydroxydlösung ml* | *Gefunden Kalzit* | |
|---|---|---|---|
| | | *mg* | *%* |
| 62.9 | 12.50 | 62.6 | 99.45 |
| 67.0 | 13.29 | 66.5 | 99.27 |
| 64.2 | 12.72 | 63.7 | 99.16 |

säure in kleinen Anteilen in den Kolben einlaufen. Die Destillation wird 15–20 Min hindurch fortgesetzt, dann wird der Inhalt des Vorlagekolbens in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 *N* Salzsäure titriert. 1 ml 0.1 *N* Salzsäure entspricht 5.0045 mg Kalzit.

Die Ergebnisse dieser Messungen sind in Tabelle II zusammengefasst.

### *Bestimmung von Oxalaten über das bei der Oxydation mittels Kaliumpermanganat gebildete Kohlendioxyd*

Die zu untersuchende Oxalatlösung soll im ml 1–2 mg Oxalat-Ionen enthalten. Im Destillationskolben werden 5 ml 5%-ige Kaliumpermanganatlösung mit 5 ml 20%-iger Schwefelsäure angesäuert. Man ergänzt das Volumen mit ausgekochtem destilliertem Wasser auf 30–50 ml, stellt den Apparat nach Zugabe von Bimsstein zusammen und kocht die Lösung aus, bzw. entlüftet den Apparat nach der bereits beschriebenen Methode. Als Vorlage werden 10.00, bzw. 20.00 ml 0.1 *N* Bariumhydroxydlösung verwendet. Durch den Hahntrichter lässt man 10.00 ml der vorbereiteten Lösung in kleinen Anteilen einlaufen und spült mit 10 und 5 ml ausgekochtem destilliertem Wasser nach. Die Zeit des Siedens richtet sich nach der Art der Bindung des Oxalats. Bei komplexen Oxalaten grosser Stabilität ist 30–40 Min hindurch fortgesetztes Sieden notwendig, beim Natriumoxalat genügen 15–20 Min. Bei den länger dauernden Destillationen muss das verdampfte Wasser mit ausgekochtem

TABELLE III

BESTIMMUNG DES NATRIUMOXALATS ÜBER DAS BEI DER OXYDATION MIT PERMANGANAT GEBILDETE KOHLENDIOXYD

| *Einwaage Na-Oxalat*[a] *g/200 ml* | *Zur Bestimmung eingemessene Lösung ml* | *Verbrauch 0.1 N $Ba(OH)_2$-Lösung ml* | | *Gefunden $Na_2(C_2O_4)$* | |
|---|---|---|---|---|---|
| | | *Einzeln* | *Durchschnitt* | *mg* | *%* |
| 0.3392 | 10.06 | 5.03<br>5.02<br>5.03 | 5.03 | 16.85 | 98.8 |
| | 5.04 | 2.52<br>2.52<br>2.53 | 2.52 | 8.44 | 98.8 |
| | 2.01 | 1.01<br>1.01 | 1.01 | 3.38 | 99.2 |

[a] 99.0%-ig. Das Präparat wurde durch direkte Bestimmung mit Kaliumpermanganat kontrolliert.

TABELLE IV

BESTIMMUNG KOMPLEXER OXALATE ÜBER DAS BEI DER OXYDATION MIT PERMANGANAT GEBILDETE KOHLENDIOXYD

| *Formel* | *$C_2O_4^{-2}$ %* | |
|---|---|---|
| | *Berechnet* | *Gefunden* |
| $K_3Cr(C_2O_4)_3 \cdot 3\ H_2O$[a] | 54.17 | 54.19 |
| $K_3Co(C_2O_4)_3 \cdot 3.5\ H_2O$[a] | 52.46 | 52.50 |

[a] Der Wassergehalt der Verbindungen wurde nach der Karl Fischer Methode kontrolliert.

destilliertem Wasser ersetzt werden. Nach beendigter Destillation wird der Inhalt des Vorlagekolbens in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 *N* Salzsäure titriert. 1 ml 0.1 *N* Salzsäure entspricht 2.2005 mg Oxalat-Ionen.

Die Ergebnisse unserer Messungen sind in den Tabellen III und IV zusammengefasst.

### *Bestimmung des Kohlendioxydgehalts von Laugen*

Vor Beginn der Bestimmung wird die Oberfläche der zu untersuchenden Lösung mit einer 4–5 mm dicken Pentanschicht bedeckt. Der Destillationskolben wird mit ausgekochtem destilliertem Wasser ausgespült und mit 5 ml Pentan beschickt. Man bringt nun einen gemessenen Anteil der zu untersuchenden Lösung in den Kolben, ergänzt mit ausgekochtem destilliertem Wasser auf 30–50 ml und stellt den Apparat nach Zugabe von Bimsstein zusammen. Das Pentan wird unter voller Kühlung in ein Becherglas abdestilliert, dann lässt man das Wasser aus dem Kühlmantel abfliessen. Das Pentan wird aus dem Becherglase ausgegossen und nachdem ein lebhafter Dampfstrom aus dem Kühlerrohr entweicht, wird die Vorlage wie üblich angebracht. Als Vorlageflüssigkeit dient der erwarteten Kohlendioxydmenge entsprechend 0.05 oder 0.01 *N* Bariumhydroxydlösung. Die zu untersuchende Lösung wird im Destillationskolben — durch den Hahntrichter — mit vorher ausgekochter 20%-iger Schwefelsäure angesäuert (nötigenfalls verwendet man 1–2 Tropfen Methylrot-Indikatorlösung).

In Tabelle V sind die Messergebnisse bezüglich des Kohlendioxydgehalts einiger Laugen zusammengefasst.

Der Apparat wurde aus „Rasotherm"-Glas hergestellt. Der Hahntrichter bzw. der Kolben sind an den Kühleraufsatz mit 11/24 bzw. 13.5/24 Normalschliffen angeschlossen. Der Apparat wird nur beim Kühler an einem Gestell eingespannt, der Kolben wird mit 2 Federn am Aufsatz befestigt. Am Aufsatz, bzw. am Kolben, befinden sich zu diesem Zwecke je 2 Glashäckchen. Ähnlich kann auch der Hahntrichter fixiert werden. Das Ende des Einlaufrohres des Hahntrichters, sowie das Ende des Kühlerrohres, sind bis auf einen Innendurchmesser von 1.5–2 mm verengt. Die Bohrung

TABELLE V

BESTIMMUNG DES KOHLENDIOXYDGEHALTS VON LAUGEN

| *Lauge* | *Eingem. Lösung ml* | *Für das $CO_2$ verbrauchte $Ba(OH)_2$-Lösung ml* | | *Gefunden $CO_2$* | |
|---|---|---|---|---|---|
| | | *Einzeln* | *Durchschnitt* | *mg* | *in äquiv. %-ten* |
| Mit CaO-Brei behandelte 1.25 *N* Natriumhydroxydlösung | 20.05 | (0.05 *N*)<br>5.85<br>5.87<br>5.84 | (0.05 *N*)<br>5.85 | 6.44 | 1.177 |
| 50%-ige (12.5 *N*) Natriumhydroxydlösung nach 24-stündiger Sedimentation | 4.99 | (0.05 *N*)<br>7.94<br>7.94<br>7.93 | (0.05 *N*)<br>7.94 | 8.74 | 0.636 |
| 0.1 *N* Bariumhydroxydlösung (5% Bariumchlorid enthaltend) | 20.00 | (0.01 *N*)<br>0.23<br>0.23<br>0.24 | (0.01 *N*)<br>0.23 | 0.051 | 0.115 |

des Hahnes im Hahntrichter ist 1–1.5 mm weit, die Hähne des Kühlers besitzen 3-mm Bohrungen. Der Innendurchmesser des Einlaufrohres des Hahntrichters beträgt 3 mm, sein Ende steht 3–5 mm über dem Boden des Kolbens. Der Hahntrichter fasst *ca.* 15 ml. Die übrigen Daten des Apparats sind aus der Abbildung ersichtlich.

## ZUSAMMENFASSUNG

Die Destillation des Kohlendioxyds lässt sich bei entsprechender Regelung der Kühlung, bei Atmosphärendruck durchführen. Die störende Wirkung des Luftkohlendioxyds wird durch Anwendung von Pentan als Sperrflüssigkeit ausgeschaltet. Im 0.1 und 0.01 *N* Massstabe lassen sich mit dieser Methode 22–0.22 mg Kohlendioxyd mit einer Genauigkeit von ±0.2–2% bestimmen.

## SUMMARY

Carbon dioxide can be distilled at atmospheric pressure if the cooling is properly controlled. A suitable procedure is described. Interference from atmospheric carbon dioxide is prevented by the use of pentane as sealing liquid. Titrations with 0.01–0.1 *N* solutions allow determination of 0.22–22 mg of carbon dioxide with an accuracy of ±2–0.2%.

## RÉSUMÉ

Une méthode est décrite pour le dosage titrimétrique de l'anhydride carbonique, avec distillation à la pression atmosphérique. Pour des teneurs en $CO_2$ de 0.22 à 22 mg, la précision est de ±2–0.2%.

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# A SPECIFIC AND SENSITIVE SPOT TEST FOR CADMIUM UTILIZING GLYOXAL-BIS(2-HYDROXYANIL)

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(Received February 17th, 1961)

Although it is a relatively common metal, cadmium has remained one of the most difficult to detect. The problems associated with its detection are apparent when it is realized that the precipitation of yellow cadmium sulfide with all of its associated complications is still considered one of the best means of detecting this element. The precipitation of the cadmium iodide complex using the iron(II) complex with $\alpha,\alpha'$-dipyridyl[1] is probably the most generally useful test reaction available up to the present. The red precipitate is so intensely colored that excellent sensitivity is obtained. Although the test is selective for anionic iodo complexes, the metals that form such complexes are those that would ordinarily be associated with cadmium and are, therefore, critical. It might be mentioned that metals such as lead, silver and thallium which are precipitated by iodide also give positive interferences due to the absorption of the reagent on the respective precipitates. Specificity can only be approached by removing the chloride group of metals and then masking other potential interfering metals as ammine complexes. Various organic reagents such as diphenylcarbazide and diphenylthiocarbazone have been employed with only moderate success. The most successful of such reagents has been *p*-nitrodiazoaminoazobenzene which forms a violet to blue lake in the presence of cadmium. Most interfering metals can be complexed by the addition of tartrate[2].

Preliminary studies of glyoxal-bis(2-hydroxyanil) disclosed its potential value as a reagent for cadmium. Excellent sensitivities were obtained, and pH control did not appear critical. A number of metals react with the reagent, but preliminary investigations indicated the likelihood that most of these could be masked through use of various complexing agents.

Under the highly alkaline conditions of the test, it was evident that tartrate would have to be present to prevent the general formation of hydroxides. In addition, the reactions of lead and thallium with the reagent were also masked with tartrate. The interference due to silver was eliminated with thiosulfate, as were reactions of copper and gold. Fluoride was used to further condition the test by masking the reactions of iron, uranium, calcium, strontium and barium.

The use of a solution of the above complexing agents gave a selective test with only cobalt, nickel and cadmium reacting. The test was made specific for cadmium by utilizing anion exchange resin beads and concentrating the metal ion on the resin as the tetraiodo complex.

## EXPERIMENTAL

### *Reagents and chemicals*

Unless otherwise specified. all solutions were made with AnalaR grade chemicals and distilled water. (*1*) Glyoxal-bis(2-hydroxyanil) solution: 1% in 95% ethyl alcohol. The reagent was prepared according to FEIGL[3]. (*2*) Piperidine: Eastman Organic (practical grade). (*3*) Masking mixture: a solution containing equal volumes of the following was prepared: (*a*) sodium thiosulfate, 20% aqueous, (*b*) sodium tartrate, 20% aqueous, (*c*) sodium fluoride, saturated aqueous. (*4*) Potassium iodide: 50% aqueous. (*5*) Metal ion solutions: stock solutions containing 10 mg/ml were prepared using appropriate salts. (*6*) Dowex 2-X8 anion exchange resin (50–100 mesh in $Cl^-$ form). A suitable quantity of resin was packed in a small column and washed with 1 *N* HCl to remove trace metal contaminants. The purified resin was then washed with distilled water and air dried.

## PROCEDURE

The following procedure is proposed. A drop of metal ion solution is placed in the depression of a white spot plate. Two drops of the masking mixture and two drops of the potassium iodide solution are added. About 20 ion exchange beads are added, and the mixture is stirred and allowed to equilibrate for a minute (the equilibration time can be varied depending upon the amount of cadmium present). The supernatant solution is then drawn from the spot plate depression and discarded. A medicine dropper, drawn to a fine point, serves nicely for this operation since care must be taken that the beads are not also drawn off. The beads are then washed three times with distilled water, the washings being drawn off and discarded as previously described. Two drops of distilled water, a drop of glyoxal-bis(2-hydroxyanil) solution and a drop of piperidine are added. A positive cadmium test is indicated by a blue color forming on the resin beads. The time of color formation and the intensity of the stain are dependent upon the amount of cadmium present. It is also to be noted that the color is not stable on the resin. Fading takes place generally within a period of several minutes.

Table I gives a list of all the ions studied in the course of this work. Of all the ions listed, only the cadmium ion gave a positive test.

To determine the extent of possible interferences from the various ions listed in Table I upon the detection of cadmium, the procedure given above was modified as follows. A drop of the metal ion solution (10 mg/ml) whose interference was to be studied was placed in the depression of a white spot plate together with a drop of cadmium solution (1 mg/ml). The remainder of the procedure was the same as that originally given.

TABLE I

IONS STUDIED FOR POSSIBLE INTERFERING EFFECTS

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Li | Na | K | Cu(II) | Rb | Ag(I) | Cs | Au(III) |
| Be | Mg | Ca | Zn | Si | Cd | Ba | Hg(I) |
| Hg(II) | Al | Ga | Ce(III) | Ce(IV) | Tl(I) | In | Y |
| Ti(IV) | Ge | Zr | Sn(II) | Sn(IV) | Pb(II) | Th | V(II) |
| V(V) | As(V) | Sb(III) | Bi(III) | Cr(III) | U(VI) | Mn(II) | Fe(III) |
| Co(II) | Ni | Ru(III) | Rh(III) | Pd(II) | Ir(IV) | Pt(IV) | Os(IV) |
| $BO_2^-$ | $CO_3^{-2}$ | $SiO_3^{-2}$ | $NO_2^-$ | $NO_3^-$ | $HPO_4^{-2}$ | $P_2O_7^{-4}$ | $S^{-2}$ |
| $S_2O_3^{-2}$ | $SO_3^{-2}$ | $SO_4^{-2}$ | $CrO_4^{-2}$ | $SeO_3^{-2}$ | $SeO_4^{-2}$ | $MoO_4^{-2}$ | $TeO_3^{-2}$ |
| $TeO_4^{-2}$ | $WO_4^{-2}$ | $F^-$ | $Cl^-$ | $ClO_3^-$ | $ClO_4^-$ | $MnO_4^-$ | $Br^-$ |
| $BrO_3^-$ | $I^-$ | $IO_3^-$ | $CN^-$ | $Fe(CN)_6^{-3}$ | $Fe(CN)_6^{-4}$ | $SCN^-$ | $NH_4$ |
| Acetate | Oxalate | Malonate | EDTA | Succinate | Tartrate | Citrate | |

A control test was run in parallel with the interference studies. The control was identical to the interference test, except that a drop of distilled water was used instead of the cadmium solution.

There were no interferences, either positive or negative, from any of the ions tested, nor did colored ions interfere.

The sensitivity of the cadmium test is given by: Limit of identification of Cd: 0.05 $\mu$g. Dilution limit: 1:1,000,000.

## DISCUSSION

Those metal ion solutions which had to be prepared in highly acidic media to prevent hydrolysis were neutralized with 6 *M* sodium carbonate solution before proceeding with the spot test.

Various bases were investigated as to their usefulness for adjusting the pH of the reaction mixture, *e.g.*, ammonium hydroxide, sodium hydroxide, pyridine, morpholine, diethylamine and piperidine. Piperidine was chosen because of its enhancement of the sensitivity of the reaction. An attempt was made to combine the glyoxal-bis-

(2-hydroxyanil) and the piperidine into a single solution, but the mixture was found to be unstable.

Preliminary tests indicated that tartrate would have to be added to prevent hydroxide formation under the alkaline conditions of the reaction. Additional observations indicated that other masking agents would be needed to further condition the test. For example, the formation of silver oxide and interferences from Cu(II) and Au(III) are masked with thiosulfate, while reactions of Fe(III), U(VI), Ca, Sr and Ba are eliminated with fluoride.

The basis for the use of the anion exchange resin is the formation of the cadmium iodo complex with its subsequent absorption on the resin. This provides an excellent method of separation from cobalt and nickel which also react with the reagent to give a red-brown and blue color respectively.

## ACKNOWLEDGEMENT

The authors acknowledge the financial support given them through the Continental Oil Company Fellowship in Analytical Chemistry.

## SUMMARY

A test for cadmium based on the use of glyoxal-bis(2-hydroxyanil) is proposed. The reaction is carried out on beads of an anion exchange resin on which the cadmium has been concentrated as the tetraiodo complex. Separations inherent in the procedure make the test specific. The limit of identification is 0.05 $\mu$g.

## RÉSUMÉ

Les auteurs proposent pour l'identification du cadmium une réaction à la touche, spécifique et sensible, au moyen de bis(2-hydroxyanil)glyoxal. La réaction s'effectue sur résine Dowex, et donne une coloration bleue.

## ZUSAMMENFASSUNG

Es wird eine Nachweisreaktion (Tüpfelprobe) für Cadmium unter Verwendung von Glyoxal-bis-(2-hydroxyanil) beschrieben. Cadmium wird als Cadmiumjodokomplex auf Anionenaustauscherharz-Perlen adsorbiert, die nach Zusatz des Reagenzes und Piperidin eine blaue Farbe annehmen.

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# Short Communication

## Determination of traces of water in gases by means of a modified Keidel electrolytic hygrometer

Using the principle suggested by Keidel[1] we have developed an electrolytic hygrometer which has distinct advantages over commercially available instruments. As is well known, the meter is based on the principle of quantitative water absorption by a phosphorus pentoxide matrix between two platinum wires spaced closely to reduce the time of response. Subsequent electrolysis of all the water absorbed converts the water to oxygen and hydrogen and continuously regenerates the phosphorus pentoxide. In the KEIDEL cell the coiled thin platinum wires are located within a narrow (diameter 1 mm) teflon capillary. This capillary, however, can easily be blocked, especially in the presence of higher olefines, which tend to polymerize under the influence of the phosphorus pentoxide. The capillary cannot readily be cleaned. This disadvantage is eliminated in our construction, in which the two platinum wires are coiled on the outside of a teflon or glass cylinder. The two shallow circular grooves, necessary for exactly spacing the two spiralized platinum wires (diameter 0.5 mm) 0.2 mm apart, can be easily turned or etched. This part of the sensing cell can be removed for cleaning purposes. Further details[2] are given in Fig. 1.

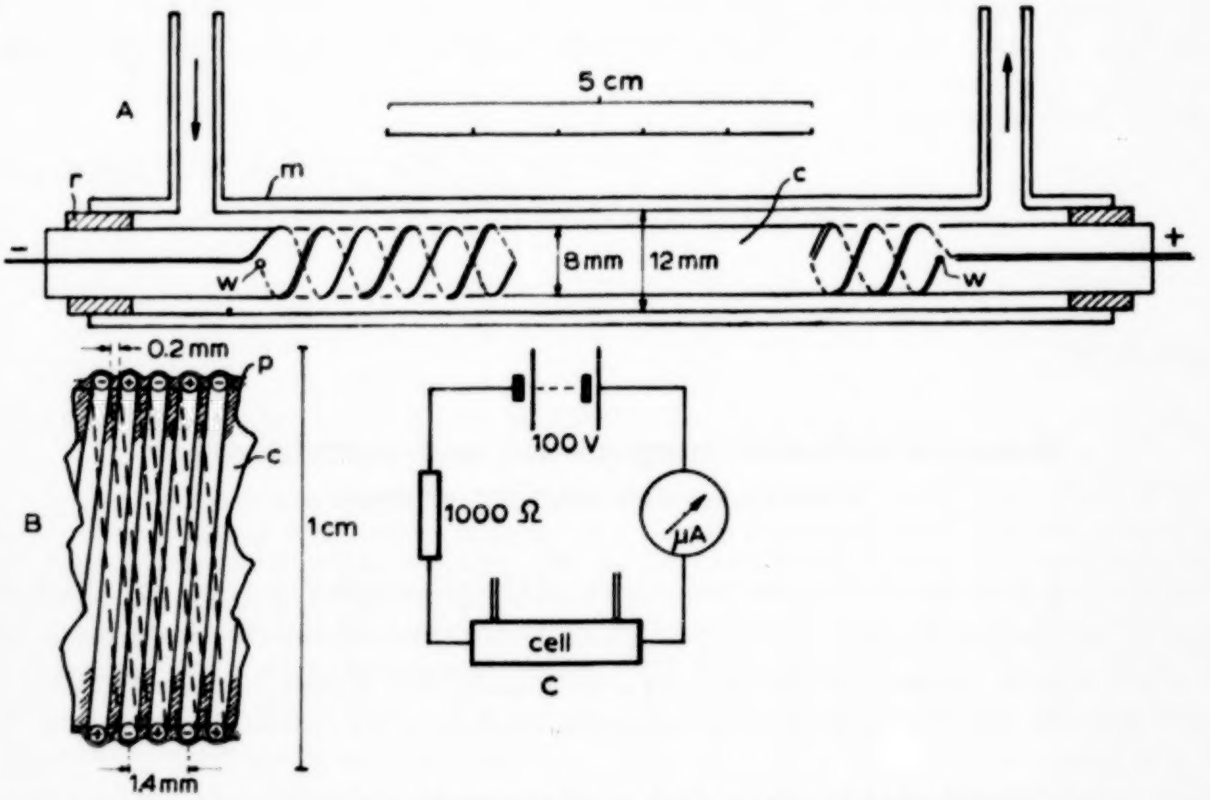

Fig. 1. Electrolytic hygrometer. A: Sensing element with enlarged detail B (longitudinal section). C: Electrical scheme. c, teflon or glass cylinder on which the two platinum wires are coiled. m, glass mantle. p, thin layer of dehydrated phosphoric acid. r, piece of butylrubber tube, attached so that no water can enter the cell. w, fixed end of the platinum wire.

### *Starting procedure*

After the platinum wires have been cleaned and made grease-proof, they are coated with a very thin film of phosphoric acid, 80–90% by weight. The cell is conditioned by electrolyzing the acid to dryness, so that the residual current amounts to some tens of microamperes. During this procedure the cell is rinsed with a stream of dry nitrogen. Normally, the cell is used with a gas flow of 100 ml/min and a working d.c. voltage of 100 V.

### *Discussion*

If the gas flow rate is constant (100 ml/min), then the current necessary to ensure complete conversion of the absorbed water to hydrogen and oxygen (one Faraday, *i.e.* 96,500 C/0.5 mole of water) amounts to 17.9 μA for each mg of water present per cubic meter gas at 760 mm and 20°. Expressing the water content in p.p.m. (v/v), this factor becomes 13.4 μA.

The range of the cell is from 5–2000 mg of water per cubic meter. Both the absorption and the electrolysis proceed with 100% efficiency, hence no additional calibration is necessary. The standard deviation is about 5%. The so-called 63%-response is achieved within 1.5 min. It is interesting to note that phosphoric acid spattering on the inner wall of the cylindrical glass mantle does not noticeably disturb the measurement. Several instruments of this type have been satisfactorily used for four years.

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[1] F. A. KEIDEL, *Anal. Chem.*, 31 (1959) 2043.
[2] *Netherlands Patent Application*, Stamicarbon N.V., Heerlen, Nr. 223,599, June 15th, 1959.

Received June 24th, 1961

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## Addendum

# Determination of magnesium and aluminium in zinc-base die-casting alloys[1]

In the above paper, brief mention was made of the possibility of applying the method described for determination of magnesium in aluminium alloys. We have since found that silica interferes in this method by causing coprecipitation of magnesium with Fe, Mn and Al. The method given (2nd paragraph, p. 239) should therefore be modified as follows.

The main constituent (aluminium) was removed by dissolving the alloy in sodium hydroxide. The insoluble residue was filtered off on paper and the residue and paper were digested with nitric and sulphuric acids, nitric acid being removed by fuming. More nitric acid was added as required to ensure complete removal of organic matter. Under these conditions, silica is insoluble. After digestion and dilution, silica was filtered off along with lead sulphate. The Fe, Mn and Al remaining were then eliminated with ammonia and ammonium persulphate, before the magnesium was determined as described originally. The addition of potassium cyanide before titration with EDTA masks any zinc which may coprecipitate with $MgNH_4PO_4 \cdot 6\ H_2O$.

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[1] L. BLOCH, *Anal. Chim. Acta*, 23 (1960) 233.

Received June 28th, 1961

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
## Vol. 25, No. 5, November 1961

### SEPARATION OF TRACES OF INORGANIC IONS FROM AQUEOUS SOLUTIONS BY GAS-, LIQUID- AND SOLID-PHASE DISTRIBUTION PROCEDURES

*(Review)*

T. S. West, *Anal. Chim. Acta*, 25 (1961) 405–421

### THE EFFECT OF HEAT ON SOLUTIONS OF CERIUM(IV) SULPHATE IN SULPHURIC ACID AND SOME ANALYTICAL IMPLICATIONS

Ceric sulphate solutions may undergo appreciable losses of cerium(IV) on heating. The overall loss is acid dependent, being at a minimum in about 1 *M* sulphuric acid, and is almost independent of the cerium(IV) concentration. Consequently as the concentration falls the actual percentage loss increases. The loss, resulting from the reaction of cerium(IV) with water, is catalysed heterogeneously at the glass surface and also on the surface of any precipitated material. The extent of the loss varies considerably with the conditions of the experiment. Solutions of ceric sulphate prepared from commercial grade cerium(IV) sulphate or ceria and from spectroscopically pure ceria, behave in the same fashion. The effect of added silver(I), copper(II), mercury(II) and phosphite ions in the cerium(IV)–water reaction is reported.

D. Grant and D. S. Payne, *Anal. Chim. Acta*, 25 (1961) 422–428

### EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

#### II. DETERMINATION OF COPPER, NICKEL, IRON, CHROMIUM AND VANADIUM

A method for the determination of nickel, copper, iron, chromium and vanadium by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending on the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the determination of these metals in highly coloured aqueous solutions. The maximum expected error is of the order of 1%, and in the majority of determinations the error is 0.5% or less.

A. J. Cameron and N. A. Gibson, *Anal. Chim. Acta*, 25 (1961) 429–433

## OXIDIMETRIC DETERMINATION OF URIC ACID WITH POTASSIUM IODATE OR PERIODATE

*(in French)*

Uric acid is determined by potentiometric titration with potassium iodate or periodate in solutions containing hydrochloric acid. Depending on the acid concentration the reagent is reduced to iodine monochloride, or to elementary iodine (in the case of iodate).

A. Berka, *Anal. Chim. Acta*, 25 (1961) 434–437

## APPLICATION OF SELENIUM SALTS IN INORGANIC ANALYSIS

The gravimetric determination of metals as selenides is proposed. Owing to the rapid atmospheric oxidation of sodium selenide and the toxic nature of hydrogen selenide, special apparatus is required. The methods are analogous to precipitation of sulphides. Arsenic, tin, antimony, platinum, ruthenium, palladium, rhodium, rhenium, mercury, silver and gold can be determined. The thermolysis of precipitates formed with arsenic, antimony, mercury, silver, rhenium, platinum, ruthenium, palladium and rhodium has been studied.

I. K. Taimni and R. Rakshpal, *Anal. Chim. Acta*, 25 (1961) 438–447

## ELIMINATION OF DISTILLATION IN THE KJELDAHL METHOD FOR THE MICRO- AND SEMIMICRO-DETERMINATION OF NITROGEN IN NITRO, NITROSO AND AZO COMPOUNDS

A method is described for the determination of nitrogen in nitro, nitroso and azo compounds by a Kjeldahl method without distillation. The compound is reduced with glucose or zinc in methanol and hydrochloric acid. The ammonium sulphate produced after the usual digestion is determined by hypochlorite–arsenite titration. A single vessel is used for reduction, digestion and titration.

M. Ashraf, M. K. Bhatty and R. A. Shah, *Anal. Chim. Acta*, 25 (1961) 448–452

## CATION-EXCHANGE BEHAVIOR OF CALCIUM ON DOWEX 50W-X8

### SEPARATION FROM MIXTURES

The cation-exchange behavior of calcium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid are examined as eluants. Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II), iron(III) and from barium. Separation factors for barium–calcium and barium–strontium are evaluated.

S. K. Majumdar and A. K. De, *Anal. Chim. Acta*, 25 (1961) 452–456

## A CONTINUOUS FLOW MONITOR FOR SCANNING $^{32}$P-CONTAINING EFFLUENTS FROM CHROMATOGRAPHY COLUMNS

A continuous flow monitor for scanning $^{32}$P-containing effluents from chromatography columns is described. The separation of $^{32}$P-labeled compounds from barley is presented as an illustration of the results obtained with the system.

A. R. Krall and L. P. Zill, *Anal. Chim. Acta*, 25 (1961) 457–460

## DETECTION OF CARBAMATE-FORMING METALS IN PRESENCE OF ALUMINIUM AND OTHER METALS BY RING OVEN AND SPOT COLORIMETRY. I.

*(in German)*

Small amounts of cations yielding insoluble dithiocarbamates are fixed on filter paper by precipitation with Na-DDTC. Other cations are removed by washing. On the Weisz-Ring oven, the metal-DDTC is moved to the ring by washing with pyridine *without* prior drying. Identification is carried out in the ring zone, if necessary after destruction of carbamate and removal of interfering cations. Cu–Al is given as example.

H. Malissa and L. J. Ottendorfer, *Anal. Chim. Acta*, 25 (1961) 461–462

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## SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM WITH SOLOCHROMATE FAST RED

A method is described for the spectrophotometric determination of micro amounts of uranyl ions with the azo dye, Solochromate Fast Red, which reacts with uranium(VI) in acetate-buffered methanol solution to form an orange-brown colored complex with maximum extinction at 490 m$\mu$. Beer's law is obeyed over a wide range of uranium concentrations. Only a limited number of foreign ions interfere, hence this method is generally applicable after removal of interfering ions by anion exchange; *e.g.* uranium can be determined in marine materials.

J. Korkisch and G. E. Janauer, *Anal. Chim. Acta*, 25 (1961) 463–469

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## SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM WITH STANNOUS IODIDE REAGENT

Iridium ions react with tin(II) iodide reagent to form a stable complex with an absorption maximum at 446 m$\mu$. Beer's law is not obeyed but the reaction is reproducible and the absorbancy is proportional to iridium concentration with an accuracy of $\pm 0.9\%$ over the range 0.8–11.7 p.p.m. Prior separation of iridium from rhodium and other transition metals is necessary. The procedure compares favorably with the tin(II) bromide method. The tin(II) halide reactions with platinum group metals are shown to diverge from true homologous series.

E. W. Berg and H. L. Youmans, *Anal. Chim. Acta*, 25 (1961) 470–475

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## SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

Cobalt(III) forms a water-soluble complex with complexone IV. The violet complex has an absorbance maximum at 545 m$\mu$ and obeys Beer's law from 1 to 100 $\mu$g cobalt per ml. The complex is easily prepared and a procedure for the spectrophotometric determination of cobalt in acid medium is given. In this method only large amounts of chromium cause significant interference. The complex contains the cobalt and the reagent in a ratio of 1 : 1, the molar extinction coefficient is 305 and the stability constant of the complex is $8.5 \cdot 10^{21}$.

E. Jacobsen and A. R. Selmer-Olsen, *Anal. Chim. Acta*, 25 (1961) 476–481

## VOLTAMMETRY AT INERT ELECTRODES

### II. CORRELATION OF EXPERIMENTAL RESULTS WITH THEORY FOR VOLTAGE AND CONTROLLED POTENTIAL SCANNING, CONTROLLED POTENTIAL ELECTROLYSIS, AND CHRONOPOTENTIOMETRIC TECHNIQUES. OXIDATION OF FERROCYANIDE AND *o*-DIANISIDINE AT BORON CARBIDE ELECTRODES

An exhaustive study of linear diffusion techniques has been carried out at $B_4C$ electrodes. In addition to proving the utility of $B_4C$ electrodes for both practical and theoretical investigations, some novel inter-relationships between modern electrochemical techniques have been developed, and the validity of the RANDLES–SEVCIK equation has been established for slow scan rates.

TH. R. MUELLER AND R. N. ADAMS, *Anal. Chim. Acta*, 25 (1961) 482–497

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## SEPARATION BY VOLATILIZATION OF THE RADIOISOTOPES OF PLATINUM, IRIDIUM, OSMIUM AND RHENIUM FORMED BY BOMBARDMENT OF A GOLD TARGET

*(in French)*

The radioactive isotopes of mercury, platinum, iridium, osmium and rhenium — products of bombardment processes in gold irradiated with protons at 150 MeV — are separated cleanly by distillation in a stream of argon or chlorine and by condensation in a tube possessing a temperature gradient.

J. MERINIS AND G. BOUISSIÈRES, *Anal. Chim. Acta*, 25 (1961) 498–504

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## NOTE ON THE VERY SENSIBLE DETECTION OF PERMANENT GASES BY GAS CHROMATOGRAPHY BY MEANS OF A METASTABLE HELIUM DETECTOR

*(Short Communication; in French)*

J. SERPINET, *Anal. Chim. Acta*, 25 (1961) 505–506

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## THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

*(Short Communication)*

E. VAN DALEN AND S. BALT, *Anal. Chim. Acta*, 25 (1961) 507–508

**Review**

# SEPARATION OF TRACES OF INORGANIC IONS FROM AQUEOUS SOLUTIONS BY GAS-, LIQUID- AND SOLID-PHASE DISTRIBUTION PROCEDURES*

T. S. WEST

*Chemistry Department, University of Birmingham (Great Britain)*

(Received April 4th, 1961)

The determination of trace amounts of inorganic constituents in solutions of commercial materials and particularly in the analysis of pure metals for atomic plants, semiconductor materials for the electrical industry, etc. is a key problem in modern analytical chemistry. In the majority of instances, satisfactory chemical or instrumental methods are available for the determination of microgram or even submicrogram amounts of ions provided that they can be supplied to the reaction vessel or instrument in a suitable chemical form. Usually this means that as far as possible, they should be presented in a relatively pure solution free from the bulk constituent and with the minimum amount of indifferent electrolyte. Consequently it is desirable to separate or concentrate the minor constituents away from the bulk material by a phase separation process, *i.e.*

$$\text{Sample} \rightarrow \underset{[\text{Phase I}]}{\text{Bulk constituent}} + \underset{[\text{Phase II}]}{\text{trace}}$$

In addition it is generally desirable that the trace should be removed into the second phase leaving the bulk constituent behind in the original medium, since this is usually a sounder proposition experimentally and it permits the operation of a concentration stage. There are of course many exceptions to such a generalisation. For example, in the determination of impurities in silica in many cases the bulk constituent may be removed as volatile silicon fluoride by treatment with hydrofluoric acid. Similarly in determining traces of other substances in tin salts advantage may be taken of the volatility of stannic iodide to remove the tin and leave the traces behind; and yet again, in the analysis of elements such as sulphur in steel[1] ferric chloride may readily be extracted into amyl acetate leaving the sulphur as sulphate in virtually pure solution ready for rapid complexometric determination.

However, these are exceptional examples of removal of a bulk constituent and subsequently throughout this paper only the removal of the trace constituent is considered. Separation by the newer techniques of ion-exchange or chromatography in any of its many forms is precluded from this discussion, which is therefore concerned with what might be termed the classical separation methods, *viz.* removal of the trace in a second phase, which can therefore only be gas, liquid or solid.

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* Paper read at 14th Annual Symposium on Analytical Chemistry, Louisiana State University, 26 Jan. 1961.

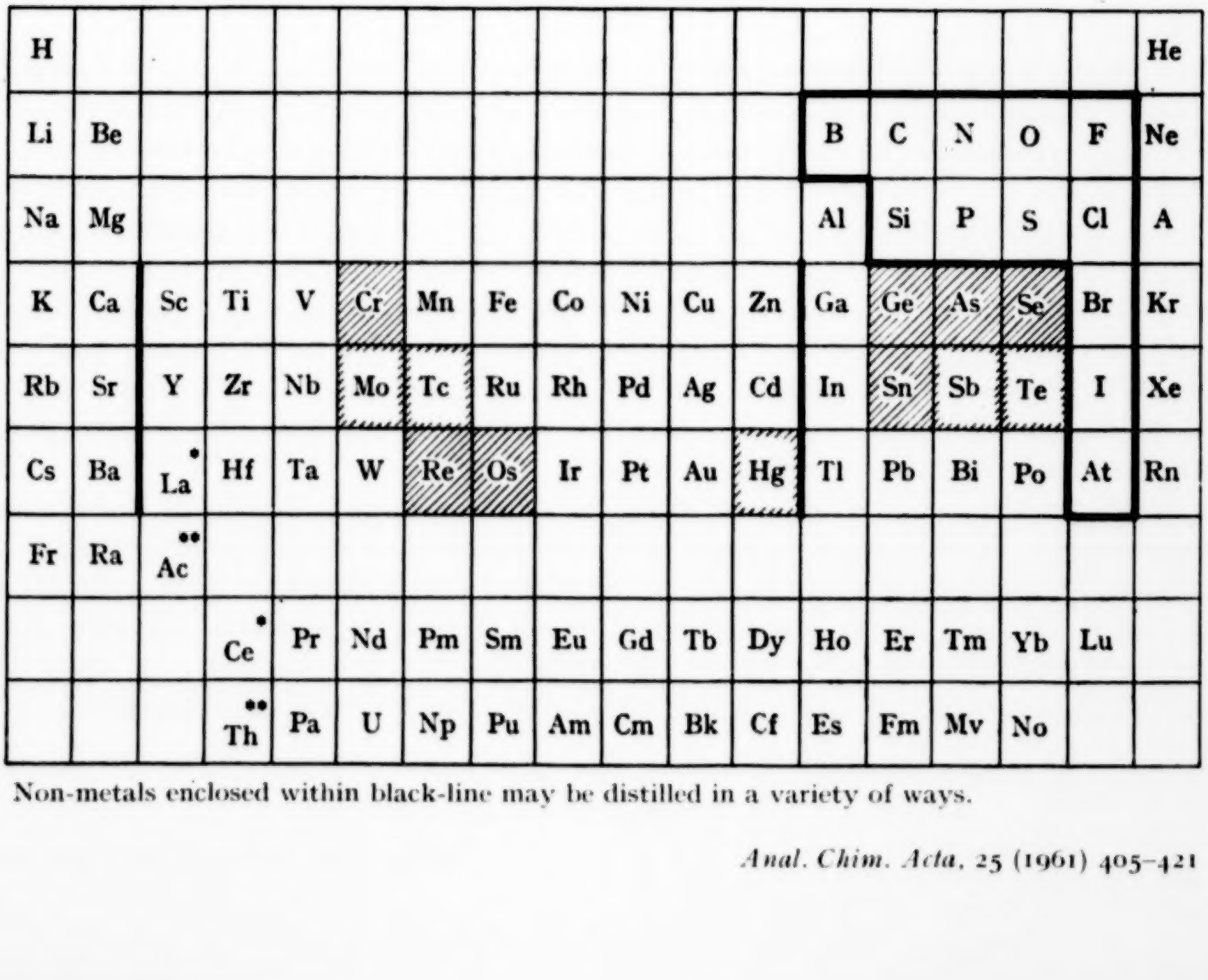
Before considering these three methods in order, it should be stated here that the following discussion is in no way intended to be exhaustive. The relevant information is scattered widely throughout the literature and the present choice mainly reflects the interests of the author. It should also be stressed at this point that little systematic work has been done on the evaluation of separation methods on a comparative basis. Many conflicting claims exist and whilst these have been avoided largely in the following paragraphs, this has not always been possible. In several instances also it has not been made clear in the original papers what the upper and lower limits of separation are. This is not entirely surprising when it is remembered that the separation procedures merely appear as a means towards an end in most analytical papers. On the whole, however, most of the following procedures are valid for $\mu g$ ($10^{-6}$ g) amounts and a considerable number also for millimicrogram ($10^{-9}$ g) or smaller amounts. Such small quantities are of course physically invisible to the unaided human eye.

## GAS PHASE SEPARATIONS

It is well known that most of the non-metals can be separated from aqueous solutions as volatile products. For example, boron may be removed as steam-volatile boric acid or as methyl borate, carbon as carbon dioxide, nitrogen as ammonia or various oxides, sulphur as hydrogen sulphide, etc. This requires little further comment. For minute amounts it is advantageous to use a carrier gas from which the trace can be isolated by chemical or physical absorption or by differential freezing. It is less generally appreciated, however, that several metals and metalloids can also be isolated by distilla-

TABLE I

ELEMENTS CONCENTRATED BY DISTILLATION FROM $HCl-HBr$ ($t = 220°$)*



| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La • | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | Ce • | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th •• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

* Non-metals enclosed within black-line may be distilled in a variety of ways.

tion or evolution from an aqueous phase. This presents a fairly selective separation of these few metals from most others, but even within the group a certain degree of selectivity of separation can be achieved by physical and chemical control of the medium. Table I summarises the volatilisation of chlorides and bromides[2] from a medium containing three other common mineral acids, *viz.* perchloric, sulphuric and phosphoric, in the temperature range 200–220°. Chromium distils quantitatively from perchloric acid either as bromide or chloride. Ruthenium and osmium behave in exactly the same way and none of the three appears to distil at 220° either as chloride or bromide from a sulphuric acid medium. On the other hand antimony distils quantitatively as bromide from either sulphuric or perchloric acid. Phosphoric acid, however, will hold back the normally volatile chloride. Tin and germanium behave in a fashion more or less identical to antimony.

Valency control is also an effective means of increasing the selectivity in many cases. In the last example for instance, 100% recovery of arsenic(III) chloride can be obtained from sulphuric acid, but only 5% of arsenic(V). Both valence forms yield quantitative recovery as bromides. Within this same framework, the separation of two closely similar elements may perhaps be mentioned.

*Osmium–ruthenium.* A medium of 5 $M$ nitric acid treated first of all with hydrogen peroxide or ferrous sulphate yields only osmium tetroxide on distillation. Subsequent removal of any chloride ion and evaporation with a sulphuric–perchloric acid medium will cause quantitative distillation of $\mu$g amounts of ruthenium.

*Arsenic–antimony*[3,4]. At a temperature $\leqslant 107°$ only arsenic(III) chloride will distil. The antimony will distil subsequently on raising the temperature. Hydrazine is recommended to maintain the valence of the arsenic throughout the process. Germanium, if present, accompanies the arsenic(III).

These few examples alone are chosen to typify this method of separation. Generally an alternative procedure would be attempted because on the whole the chemical background and manipulative technique of distillation is more difficult than that of the other techniques which follow. However, the use of organic reagents has scarcely yet entered this branch of separation chemistry, though the volatilisation of methyl borate is a well known example. It is recognized that several metal chelates *e.g.* the acetylacetonates of several metals may be distilled without decomposition and the volatility of certain 8-hydroxyquinoline metal-ion compounds is a source of difficulty in many analytical experiments. The entry of organic reagents into this region may well revolutionise our approach to the use of this rather selective separation technique.

## SOLVENT EXTRACTION

If the second phase which is to be separated off from the aqueous solution is itself a liquid phase then we are most certainly concerned with the preferential partition of the inorganic trace-ion across a liquid–liquid phase boundary into a water-immiscible organic solvent. The phenomenon of precipitation of a non-miscible liquid phase from an aqueous solution of inorganic ions is practically unknown.

A cation in aqueous solution exists largely as an aquo-ion complex with all possible free coordination positions occupied by water molecules. This and any secondary aggregation of water molecules results in a water-jacketed ion which, whether we consider things fundamentally on the basis of Hildebrand's theory of regular solutions[5] in terms of solubility parameters, etc., or on the simple rule-of-thumb dictum that 'like dissolves like', tells us that such ions have little chance of punching a hole in the liquid–liquid interface to pass through and mix smoothly with the organic molecules which almost certainly will have a much lower dielectric constant.

In order to make the ion pass the phase boundary it is necessary to divest it of all or most of its water molecules and replace them by other firmly coordinated groups which, when bound to the ion, possess the minimum of ionic character. The groups (ligands) will coordinate in a stepwise fashion if unidentate in character or if multidentate will coordinate in a smaller number of steps according to the requirements of the ion. In the latter case the entropy effect of the replacement of two or more water molecules by only one of reagent and the inherent strength of subsequent ring closure is likely to result in circumstances more favourable for successful extraction.

It can readily be shown, after making certain simplifying assumptions concerning the equilibria involved, that the ratio of the total of metal-ion species in the organic phase to the total of metal-ion species in the aqueous phase can be related very conveniently to the fundamental parameters of the system by the expression

$$D = \frac{K_C K_{CD} K_R{}^n}{K_{RD}{}^n} \cdot \frac{[\mathrm{HR}]_0{}^n}{[\mathrm{H}^+]^n_{\mathrm{Aq}}}$$

*i.e.*

$$D = k' \cdot [\mathrm{HR}]^n_0 / [\mathrm{H}^+]^n_{\mathrm{Aq}}$$

where $D$ is the distribution ratio, $K_C$ is the instability constant of the extracting species $MR_n$, $K_{CD}$ is the partition coefficient of the extraction species, $K_R$ is the acid dissociation constant of the protonated form of the ligand *i.e.* HR, $K_{RD}$ is the partition coefficient of the ligand $R^-$, $[\mathrm{HR}]_0$ is the concentration of the protonated ligand in the organic phase, $[\mathrm{H}^+]$ is the concentration of hydrogen ion in the aqueous solution and $n$ represents the number of $\mathrm{R}^-$ groups coordinated to each metal ion (M).

Splitting this expression into two parts as shown, it is apparent from that in choosing a reagent the stability constant ($k'$) should be as high as possible, the partition coefficient of the complex as high as possible and the acid strength of the protonated ligand also as high as possible (*i.e.* $\mathrm{R}^-$ should have a low affinity for $\mathrm{H}^+$), and finally the distribution coefficient of the free ligand should be as low as possible. The last mentioned two factors are particularly important since they may operate through the exponent $n \geqslant 1$.

Taking the second half of the expression into account it is apparent that once the reagent has been selected, the acidity of the aqueous phase $[\mathrm{H}^+]_{\mathrm{Aq}}$ should be minimal and the concentration of the acid species of the reagent in the organic phase as high as possible.

If two metals extract simultaneously then the separation which may be expected between them is defined by the separation factor $\beta$: $\beta = D_1/D_2$ where $D_1$ and $D_2$ are the appropriate distribution ratios, $D = \Sigma[\mathrm{M}]_{\mathrm{org}}/\Sigma[\mathrm{M}]_{\mathrm{Aq}}$.

The law of electrical neutrality is a good peg on which to hang any chemical calculation. In the instance of extraction, it clearly indicates that whereas a cation may readily pass a phase boundary if it is locked up in an undissociated neutral molecule, it cannot pass in the ionic form (cationic or anionic) unless it takes with it an equal charge concentration of the opposite polarity, *i.e.* it must pass in association with other counter ions.

This type of system is known as an ion-association system. Neutral molecules may usually be classified within the chelate extraction system since most organic reagents contain both ionogenic and coordinating groups in such a way that the principal valence and coordinate requirements of the ion are simultaneously satisfied by the reagent. This results in a neutral molecule with no attached water groups.

### *Ion-association systems*

The extraction of most inorganic ion-association systems is found to depend markedly on the nature of the extracting solvent. This is so because most of these systems still have the ion bound to some remaining coordinated water molecules (similarly with the counter-ion) and usually it is the case that it is possible for these to be replaced by molecules of oxygen-containing organic solvents such as ethers, ketones, esters, alcohols, etc. Once these solvent molecules are bound to the extracting ions it is not difficult to understand why the latter may then pass the phase boundary to intermingle smoothly with the solvent molecules. The similarity of molecular structure also explains why most ion-association systems extract well at high concentration. The selective nature of the solvent can be explained on several grounds, but one of the chief factors appears to be stereochemical. In practice this appears to be more important than the basicity of the oxygen atoms. Thus on the grounds of basicity one would predict an order of efficiency of alcohols $>$ ethers $>$ ketones, but the steric factor introduced by the more accessible promontory position of a carbonyl as opposed to a chain-linked oxygen results in ketones being generally preferable to ethers.

It is also found that the addition of fairly large amounts of electrolyte frequently aids the extraction. These added electrolytes can of course act through a common-ion action, but frequently this is not the most important factor. The binding up of a large proportion of the available water molecules in the aqueous solution within the coordination spheres of the ions of the salting-out agent appears to be a much more decisive item and also the considerable lessening of the dielectric constant of the aqueous solution. This last factor greatly favours ion-pairing, etc.

*Chloride ion systems.* The chloride ion system was used in 1892 by ROTHE[6] for the ether extraction of ferric chloride from a strong hydrochloric acid system. Many elements extract well from hydrochloric acid into a variety of oxygen-containing organic solvents, *e.g.* Sc, Fe, Ga, Ge, As, Nb, Mo, Sb, Pt, Au, Tl, Po, Pa, all *ca.* 100% with large amounts of Hg, V, Sn, Te and small amounts (*ca.* 1%) of Co, Ni, In, and Ir, whilst others such as Cu, Zn, Mn, Cr, Zr, Ag, Pb, Cd, Bi are unaffected.

Within the group of extractable ions, selectivity can be introduced by chemical control of the medium. Thus the lower oxidation states of iron, thallium and antimony do not extract appreciably whilst upon oxidation it is found they all extract efficiently. The reverse is true for elements such as tin, and arsenic. Then again, at low acidity the extraction of iron(III) is negligible, but gold(III) and mercury(II) extract well. When the acidity is raised mercury(II) no longer extracts, but iron(III) does whilst gold still extracts. The influence of solvent choice may be cited for the cobalt/nickel system. If the acidity is controlled at 4.5 $M$ a separation factor $\beta_{Co/Ni}$ of 70 can be achieved with *n*-octanol[7].

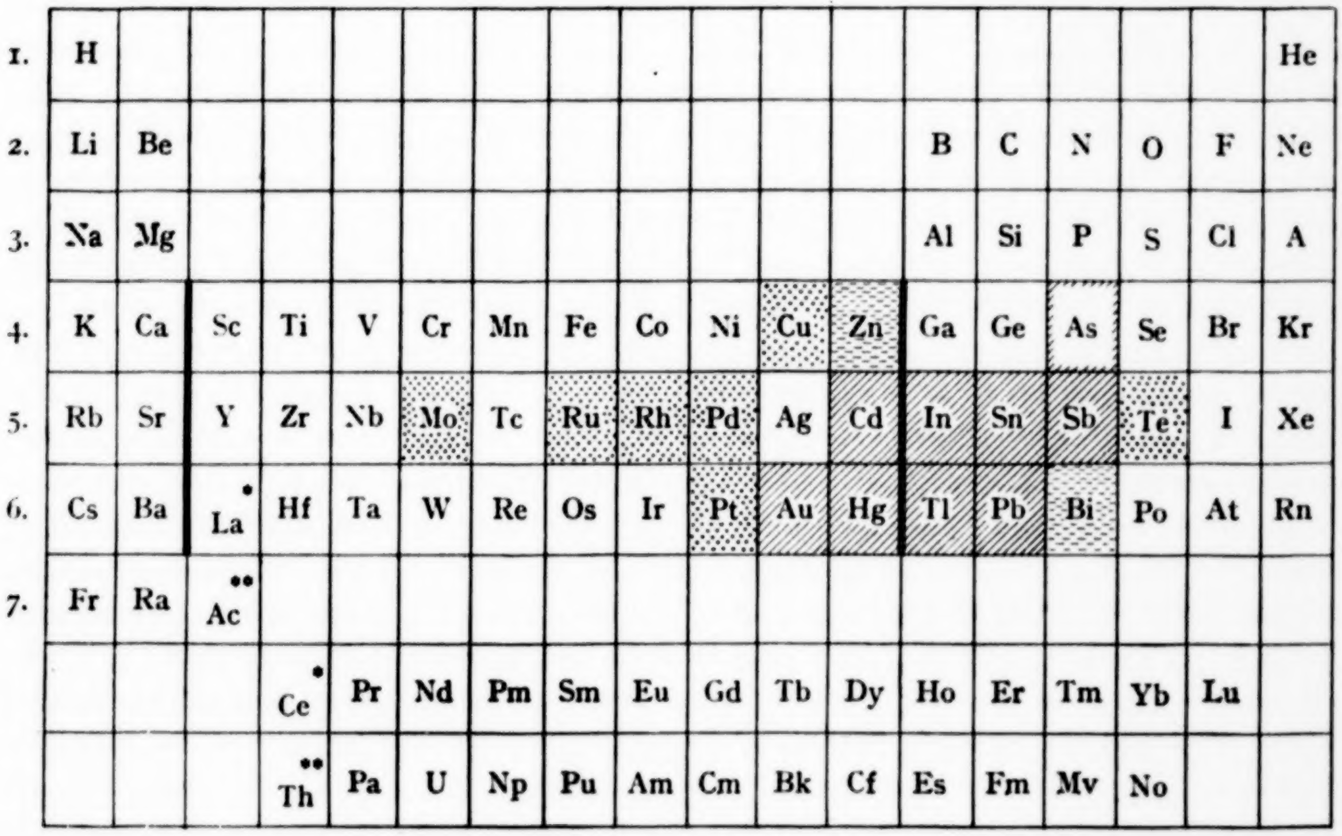
*Bromide ion systems* tend to be more selective in nature. The group 3b elements

Ga, In, Tl all extract well, as do Fe, Au, Hg and, to a lesser extent (>50%), As, Sb, Sn. Moderate extraction (*ca.* 30%) occurs with Se, Mo and small amounts (*ca.* 1%) of Cu, Zn, Pd, Te and Pt also partition. Again chemical control enhances selectivity. Thus Fe, Cu and Tl are favoured in the oxidised state, but scarcely extract following reduction. The situation is reversed for Pt. Acidity control is also effective as before.

*Iodide ion systems.* The behaviour of iodide ion systems is summarised in Table II. In this case it is noticeable that lead and cadmium now extract well. Some authors find iron to extract[8] whilst others do not[9]. With this system it is convenient to work with an acidified solution of potassium iodide instead of with free hydriodic acid.

TABLE II

ELEMENTS EXTRACTED FROM IODIDE ION-ASSOCIATION SYSTEMS



| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu ▒ | Zn ▤ | Ga | Ge | As ☐ | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo ▒ | Tc | Ru ▒ | Rh ▒ | Pd ▒ | Ag | Cd ▨ | In ▨ | Sn ▨ | Sb ▨ | Te ▒ | I | Xe |
| 6. | Cs | Ba | La • | Hf | Ta | W | Re | Os | Ir | Pt ▒ | Au ▨ | Hg ▨ | Tl ▨ | Pb ▨ | Bi ▤ | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | Ce • | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th •• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Key for Tables I and II

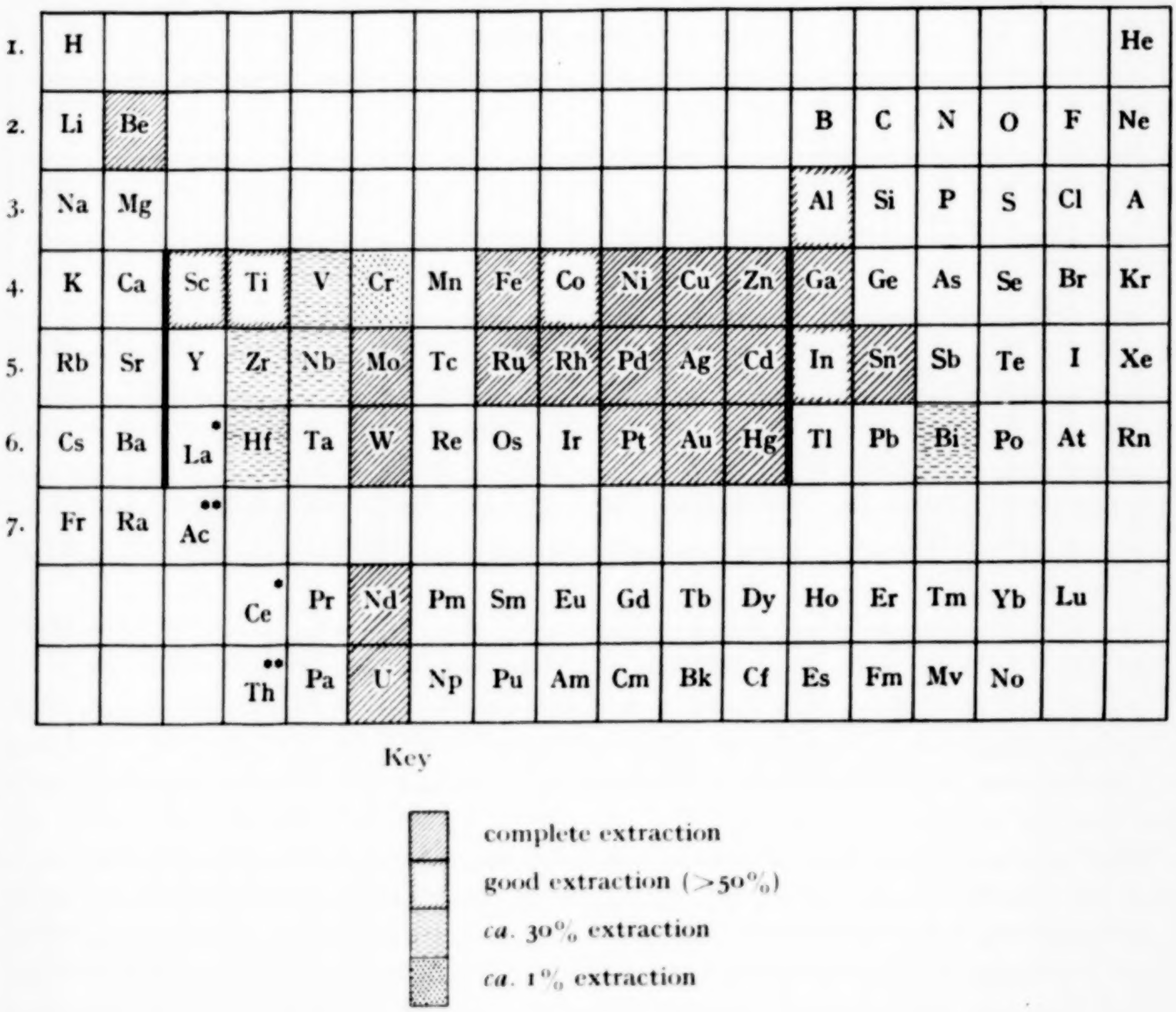
▨ complete extraction
☐ good extraction (>50%)
▤ *ca.* 30% extraction
▒ *ca.* 1% extraction

*Fluoride ion systems.* Fluoride ion association systems present the most selective separations within the halide group. Only Nb, Ta, Pa extract efficiently though some authorities found quantitative extraction of tin(II) and (IV)[10] and others disagree[11]. Further selectivity is also possible within the group, however, for a $\beta$-value of 880 is obtained[12] for the Nb/Ta system in 0.4 $M$ hydrofluoric acid. Only tantalum extracts well at this acidity.

*Thiocyanate ion systems.* Lastly the pseudo-halide thiocyanate ion system is considered since it is a suitable connecting link with chelate systems. Most ion association systems function best at very low pH when masking agents cannot usually be applied to increase selectivity. Thiocyanate and most chelate systems function better in the normal pH range (0–14) where masking and pH control are on the whole, much more effective. Table III shows the situation with thiocyanate. The system is not as unselective as appears at first sight, for remarkable changes can be brought about by masking and pH control, etc. Even two such unpromising systems as rare earths–thorium[13] and zirconium–hafnium[14,15] (extraction of the first named metals) can be resolved in this instance.

TABLE III

ELEMENTS EXTRACTED FROM THIOCYANATE ION-ASSOCIATION SYSTEMS



| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La • | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | Ce • | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th •• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Key

▨ complete extraction

□ good extraction (>50%)

▤ *ca.* 30% extraction

░ *ca.* 1% extraction

*Chelate systems.* Most of the organic reagents used in inorganic analysis for the precipitation of weighing forms may be used for extraction since the metal ions are usually fully coordinated by the reagent, surrounded by a bulky envelope of organic molecules, screened from solvent effects, etc. The nature of the solvent is much less critical with such systems and even unpromising materials such as benzene, kerosene, carbon tetrachloride, etc, may be used. With few exceptions, however, the solubility of most metal chelates in organic solvents is not very high and in contrast to ion association systems they are not suitable for bulk extractions. On the other hand, the effects due to ring formation, entropy differences, etc. all tend to make the sensitivity of such systems rather high.

*Oxine.* 8-Hydroxyquinoline is well known for its ability to precipitate some 30 cations in normal gravimetric work. Most of these chelate compounds are extractable into solvents such as chloroform under specified pH conditions, *cf.* Table. IV. Used in high concentration at high pH, even the alkaline earths will extract, thus demonstrating the validity of the $[HR]_O/[H^+]_{Aq}$ factor in the equation previously mentioned. At the pH where most of these extractions occur masking action may readily be applied. For example, cyanide ion addition prevents extraction of the strong complex formers such as iron, copper, nickel, molybdenum[16,17], but leaves others such as lead and manganese susceptible to removal. EDTA has a similar role to play with Al, Co, Mn, Fe, Ni whilst acetate ion[18] may mask thorium and iodide masks mercury(II).

TABLE IV

OXINE EXTRACTION SYSTEMS

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | ▨ Mg | | | | | | | | | | | ▨ Al | Si | P | S | Cl | A |
| 4. | K | ▨ Ca | ▨ Sc | ▨ Ti | ▨ V | Cr | ▨ Mn | ▨ Fe | ▨ Co | ▨ Ni | ▨ Cu | ▨ Zn | ▨ Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | ▨ Sr | Y | ▨ Zr | ▨ Nb | ▨ Mo | Tc | ▨ Ru | Rh | ▨ Pd | Ag | ▨ Cd | ▨ In | ▨ Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La • | ▨ Hf | Ta | ▨ W | Re | Os | Ir | Pt | Au | Hg | ▨ Tl | ▨ Pb | ▨ Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | ▨ Ce • | Pr | ▨ Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | ▨ Er | Tm | Yb | Lu | |
| | | | | ▨ Th •• | ▨ Pa | ▨ U | Np | ▨ Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Merritt and Walker's reagent[19], 8-hydroxyquinaldine, with its sterically hindering 2-methyl group is inactive towards aluminium so that a double extraction first with this reagent and subsequently with oxine[20] provides a clean separation of aluminium from practically all other metals. Further modification of the reagent can yield higher selectivity along other directions. Thus as an example, the use of 5,7-dichloro-8-hydroxyquinoline by Moeller and Jackson[21] may be quoted.

The strong fluorescence of oxine chelates is useful for determining small traces of metals, following extraction, directly in the organic phase without further processing. Concentrations at the 0.1-p.p.b. region can readily be extracted.

*Dithizone.* Dithizone extracts well in the middle ranges of the periodic table and since its potentialities are well known by virtue of the use of its tinctorial powers in absorptiometric analysis, little mention need be made of it here. It can also be rendered highly selective by masking action. Thus in presence of excess of EDTA and thiocyanate only mercury(II) is extracted by dithizone; in the presence of cyanide and thiocyanate only mercury(II) and copper(II), and in presence of EDTA (alone), mercury (II) and silver[22].

Selective phase stripping is sometimes useful for increasing selectivity. Thus if a dithizone extract contains Hg + Cu + Au + Ag shaking up of the layer in turn with the named reagent in aqueous solution causes back-extraction of the ions as follows:

$$\mathrm{Cu + Ag + Au + Hg}\left\{\begin{array}{l} \xrightarrow{\mathrm{CNS}} \mathrm{Ag} \\ \xrightarrow{\mathrm{CN}} \mathrm{Au} \\ \xrightarrow{\mathrm{EDTA}} \mathrm{Cu\,(II)} \\ \xrightarrow{\mathrm{I}} \mathrm{Hg(II)} \end{array}\right.$$

Cupferron is another excellent all-purpose extraction agent[23], whilst many other more selective extractants may be used. For example dimethylglyoxime extracts only palladium(II) in 1 *M* sulphuric acid[24], whilst only iron(II) and nickel partition from a basic pyridine medium[25]. High specificity may also be obtained by the phenanthroline and 4,7-diphenyl-1,10-phenanthroline systems (iron(II) and copper)[26] but in this instance the system involved depends on both chelation and ion-association.

### *Acetylacetone*

One further chelate system should be mentioned. This is dependent on $\beta\beta'$-diketones such as acetylacetone. Acetylacetone has been investigated extensively by Freiser and his coworkers[27]. The reagent, being virtually a water immiscible liquid, may be used as its own solvent. Consequently because of the similarity of structure between the metal–chelate and the solvent molecules, high solubility and extraction power is possible so that acetylacetone may be applied equally well to macro and micro amounts. The following metals may be extracted: Be, Ti, V, Cr, Mn, Fe, Cu. In the presence of EDTA only beryllium and uranium(VI) are extracted and on a kinetic basis chromium(III), a slow reactor, may be separated from iron(III), copper(II) and molybdenum(VI). Cobalt and nickel are not normally extracted but cobalt(III) is readily partitioned, so a separation is easily obtained between the two.

### *Extraction of anions*

Finally, mention should be made briefly of the extraction of anions as well as of cations. Only one example can be quoted here, namely the work of Smith and Page[28] on the use of N-methyl-di-*n*-octylamine in chloroform as an extractant for mineral acids from solution (*cf.* Table V).

This procedure presents a neat method of removing unwanted acidity without either increasing the ionic strength of the medium — as in neutralisation with alkali, or increasing the volume markedly — as for example in ion-exchange. Metals which exist in the anionic form can readily be extracted, *e.g.* vanadium(V) and chromium

(VI), and a separation is possible between niobium and tantalum (*cf.* Table VI) based on the selective extraction of the chloride complex of niobium by this same reagent system. Much recent work has been done along these lines and in this respect the work of F. L. MOORE and his coworkers, published mainly in *Anal. Chem.* is noteworthy.

TABLE V

EXTRACTION OF ACIDS INTO 5% METHYLDIOCTYLAMINE IN CHLOROFORM

| *Acid* | *N* | *Equivalent of amine used* | *% In aqueous layer* | *% Recovered* |
|---|---|---|---|---|
| Acetic | 0.1 | 2.0 | 3 | 90 |
| Chromic | 0.1 | 1.5 | 2 | 97 |
| Hydrochloric | 1.0 | 1.0 | 1 | 98 |
| Nitric | 0.1 | 1.2 | 0 | 98 |
| Oxalic | 0.1 | 1.2 | 4 | 98 |
| Phosphoric | 0.21 | 1.2 | 44 | 50 |
| Succinic | 0.37 | 1.0 | 11 | 90 |
| Sulphuric | 1.0 | 2.0 | 1 | 98 |
| *p*-Toluene sulphonic | 0.05 | 1.2 | 3 | 97 |

TABLE VI

EXTRACTION OF NIOBIUM AND TANTALUM BY 5% METHYLDIOCTYLAMINE IN XYLENE FROM AQUEOUS HYDROCHLORIC ACID

| *HCl M* | *% Extraction* | |
|---|---|---|
| | *Nb* | *Ta* |
| 2 | 4.0 | — |
| 2.9 | — | 0.25 |
| 3 | 2.4 | — |
| 4 | 2.2 | — |
| 4.85 | — | 0.11 |
| 6 | 21.5 | — |
| 7.28 | — | 0.55 |
| 8 | 99.3 | — |
| 8.85 | — | 1.10 |
| 9.6 | 100 | — |
| 10.10 | — | 1.35 |
| 11.2 | — | 1.40 |

Extensive reviews of solvent extraction methods are readily available[29,30].

## SOLID PHASE SEPARATION

It is often argued that precipitation is far inferior to solvent extraction as a separation process for trace amounts and this is true because all precipitates have a finite solubility and precipitation is a unit process as opposed to extraction which is dependent solely on a distribution *ratio* and may therefore be operated as a repeated batch-process or continuously. However, *direct* precipitation is not the analogue of extraction and therefore this argument against precipitation is misleading. The precipitation analogue of solvent extraction is what might be termed a solid–phase distribution technique in which the trace ion existing in solution is caused to migrate preferentially across a phase boundary into a pre-existing or newly forming *solid* phase. This technique which may more loosely be called coprecipitation is just as sensitive as solvent extraction, as will be seen from the following paragraphs.

Solid–phase distribution proceeds by virtue of several processes including: (*a*) mixed crystal formation (isomorphism) in which the extracted ion penetrates into the host crystal and mixes intimately with its molecules; (*b*) solid solution, since most crystals are possessed of some degree of mutual solubility; (*c*) chemical compound formation; (*d*) adsorption, which is largely a surface phenomenon controlled by crystal lattice forces and the nature of the liquid medium in contact with the surface; (*e*) occlusion, *i.e.* mechanical trapping or entrainment by the host-precipitate particularly when it is freshly formed *in situ*.

Before considering these various factors further it is well to state clearly that the use of host precipitates (gathering agents) allows traces of ions to be deposited from solution at concentration levels where the ion-product of the trace salt nowhere near exceeds its solubility product. Thus the technique allows separation to be achieved well below the limiting barrier of normal solubility.

A homogeneous distribution law for mixed crystal formation may readily be defined by the expression $D = K_{mx}/K_{tx}$, where $K_{mx}$ and $K_{tx}$ represent the solubility products of the host precipitate and the trace salt respectively. Obviously, for large distribution ratios the host precipitate should be considerably more soluble than the trace precipitate, but it should still be sufficiently insoluble to allow the ratio $[\mathrm{M}^{+n}]_{\mathrm{Precipitated}}/[\mathrm{M}^{+n}]_{\mathrm{Solution}}$ to be *ca.* 100. It is quite common, however, for homogeneous distribution not to be present during precipitation or even after considerable ageing. In this case the distribution in the surface layers must be considered. According to DOERNER AND HOSKINS[31] the relationship may then be expressed logarithmically as:

$$\log\frac{[t]_{\mathrm{Total}}}{[t]_{\mathrm{Solution}}} = \lambda \log\frac{[\mathrm{M}]_{\mathrm{Total}}}{[\mathrm{M}]_{\mathrm{Solution}}}$$

where $\lambda$ represents the logarithmic distribution coefficient governing heterogeneous distribution of $tX$ throughout $\mathrm{M}X$. In practice it is usually found that the behaviour of the system is intermediate between the two conditions represented by these equations.

Usually it is better to form the solid phase in the medium rather than to add it as a solid because advantage may then be taken of most of the factors involved and of course larger and more reactive surface areas may be obtained with nucleating precipitates. Furthermore, it is frequently advantageous to reverse the conditions normally obtaining in gravimetric analysis so that the precipitates are formed with maximal nucleation. The solid phase formed may be allowed, in most cases, to undergo particle growth by the process of self-induced recrystallisation caused by the relatively high solubility of the small particles.

### *Choice of collector*

The influence of the various distributing mechanisms previously mentioned on the choice of the host precipitate may be discussed very briefly. Generally *mixed crystal formation* is advantageous when it may be applied, because it tends to promote selectivity and high distribution ratios. The host precipitate should be chosen to be more soluble than the trace compound and the ionic radii of M and $t$ should lie within ± 10% of each other. Again, the choice of *compound formation* as the gathering mechanism is likely to result in group selectivity, *e.g.* the use of tellurium to collect gold — probably as telluride — results in simultaneous collection of the other noble metals. When surface adsorption is the mechanism, the PANETH–FAJANS–HAHN rule[32] indicates that if the host precipitate is brought down with an excess of $M^{+n}$ ions and is more soluble than $tX$ then exchange of M and $t$ ions will tend to occur at the surface, even though the solubility product of $tX$ has not been exceeded. In the case of *mechanical trapping*, a voluminous precipitate is obviously advantageous. If the host crystals are soft (low surface tension) then ageing will at least not be harmful, but if they are hard and of high surface tension then the ratio of the solubility of the small primary particles of precipitate to those of the massive crystal ($S_r/S$) will be high as shown in the equation[33],

$$\frac{RT}{M}\,{}^{e}\log\frac{S_r}{S} = \frac{2\sigma}{dr}$$

where $S_r$ denotes the solubility of a small particle of radius $r$; $S$ the solubility of massive crystals of precipitate, $\sigma$ the surface tension, $d$ the density and $M$ the molecular weight, so that ageing will promote considerable crystal growth and liberation of occluded trace material. $S_r/S$ for barium sulphate crystals of radius 0.02 is *ca.* 600 whilst for calcium sulphate it is only *ca.* 3.

The subsequent treatment of the trace may also of course determine the choice of the host precipitate. In this respect, volatile compounds such as those of Hg, As, Sb, Sn may be most useful. The host phase may be filtered or centrifuged off in the usual way, but if the amount is small it may be advantageous to form the collecting

TABLE VII

CATIONS CONCENTRATED BY ZnO ADDITION

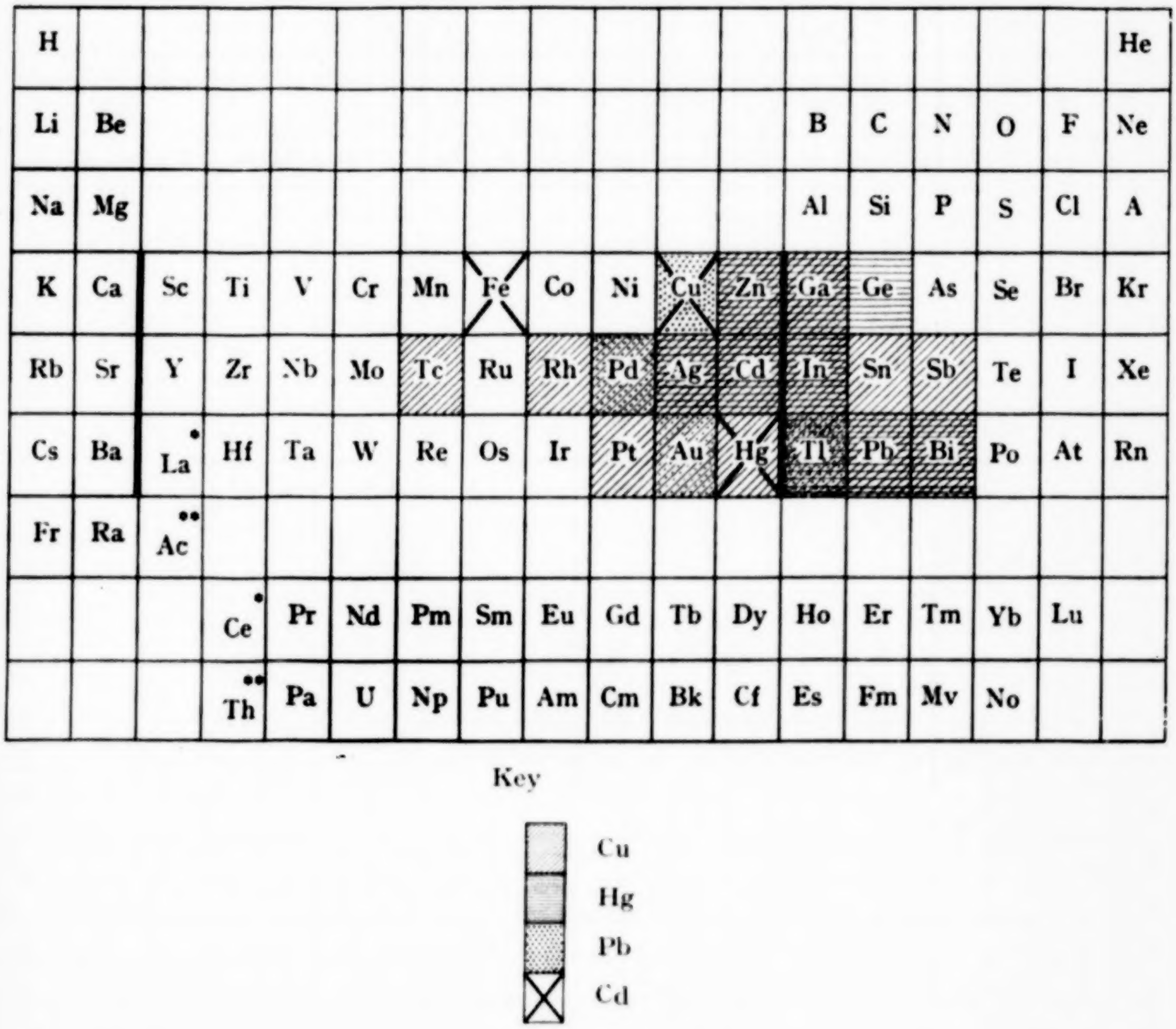
| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | ▨ Ti | ▨ V | ▨ Cr | ▨ Mn | ▨ Fe | ▨ Co | Ni | ▨ Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | ▨ Zr | ▨ Nb | ▨ Mo | Tc | Ru | Rh | Pd | Ag | Cd | ▨ In | Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La • | ▨ Hf | ▨ Ta | ▨ W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | Ce • | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th •• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

precipitate in the interstitial spaces of a filter paper. Thus for example cadmium sulphide may be used in this way to collect traces of copper in nickel or lead salts when these are dissolved up and the copper is only at the p.p.b. level[34].

The collection of traces by this technique has been reviewed recently by SANDELL[35] and elsewhere by the author[36]. Both these reviews approach matters from the viewpoint of the metal being concentrated. In the rest of this paper some (by no means all) of this information is collated from the viewpoint of the collector being used. It is presented largely in tabular form for ease of consultation, but this may obscure the measure of selectivity that is frequently possible by control of the experimental conditions.

TABLE VIII

CATIONS CONCENTRATED ON SULPHIDES OF Hg, Cu, Pb AND Cd



| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La • | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac •• | | | | | | | | | | | | | | | |
| | | | | Ce • | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th •• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Key

░ Cu

▒ Hg

▓ Pb

☒ Cd

*Zinc oxide.* Zinc oxide is mentioned first since it is more often than not added in the solid state to the solution containing the trace ion. Its use is thus more closely related to solvent extraction than that of most other collectors which are normally formed freshly by direct precipitation in the medium containing the trace. As a recent example of its use, mention may be made of the work of REYNOLDS AND SHALGOSKY[37] on the determination of traces of indium in cadmium in the 1–10 p.p.m. range.

TABLE IX COLLECTION OF VARIOUS IONS ON THE HYDROXIDES OF (a) ALUMINIUM, (b) IRON(III) AND (c) MANGANESE(IV)

(a)

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | ▨ Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | ▨ Ti | ▨ V | ▨ Cr | Mn | ▨ Fe | ▨ Co | ▨ Ni | Cu | ▨ Zn | ▨ Ga | ▨ Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | ▨ Zr | ▨ Nb | ▨ Mo | Tc | ▨ Ru | ▨ Rh | Pd | Ag | Cd | In | ▨ Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | ▨ La• | ▨ Hf | Ta | ▨ W | Re | Os | ▨ Ir | ▨ Pt | Au | Hg | Tl | Pb | ▨ Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac•• | | | | | | | | | | | | | | | |
| | | | | Ce• | Pr | Nd | Pm | Sm | ▨ Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th•• | Pa | ▨ U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

(b)

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | ▨ Mg | | | | | | | | | | | ▨ Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | ▨ Ti | ▨ V | ▨ Cr | ▨ Mn | Fe | ▨ Co | ▨ Ni | Cu | ▨ Zn | Ga | ▨ Ge | ▨ As | ▨ Se | Br | Kr |
| 5. | Rb | Sr | Y | ▨ Zr | Nb | ▨ Mo | Tc | ▨ Ru | ▨ Rh | Pd | Ag | ▨ Cd | In | ▨ Sn | Sb | ▨ Te | I | Xe |
| 6. | Cs | Ba | La• | Hf | Ta | ▨ W | Re | Os | ▨ Ir | ▨ Pt | Au | Hg | ▨ Tl | Pb | ▨ Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac•• | | | | | | | | | | | | | | | |
| | | | | Ce• | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | ▨ Th•• | Pa | ▨ U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

(c)

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | ▨ Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | ▨ Cr | Mn | ▨ Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | ▨ Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | ▨ Sn | ▨ Sb | Te | I | Xe |
| 6. | Cs | Ba | La• | Hf | Ta | W | Re | Os | Ir | Pt | ▨ Au | Hg | ▨ Tl | Pb | ▨ Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac•• | | | | | | | | | | | | | | | |
| | | | | Ce• | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | ▨ Th•• | ▨ Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

## TABLE X

### CATIONS CONCENTRATED ON COPPER OXINATE

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | ▨ Mg | | | | | | | | | | | ▨ Al | Si | P | S | Cl | A |
| 4. | K | ▨ Ca | Sc | Ti | V | Cr | ▨ Mn | ▨ Fe | Co | Ni | ▨ Cu | ▨ Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | ▨ Cd | In | Sn | Sb | Te | I | Xe |
| 6. | Cs | Ba | La• | Hf | Ta | W | Re | Os | Ir | Pt | Au | ▨ Hg | Tl | Pb | Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac•• | | | | | | | | | | | | | | | |
| | | | | Ce• | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th•• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Cu on Pb oxinate; Ca with oxine only.

## TABLE XI

### CATIONS CONCENTRATED BY METHYL VIOLET–IODIDE SYSTEM

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | H | | | | | | | | | | | | | | | | | He |
| 2. | Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 3. | Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| 4. | K | Ca | Sc | Ti | V | Cr | Mn | ▨ Fe | Co | ▨ Ni | ▨ Cu | ▨ Zn | Ga | Ge | As | Se | Br | Kr |
| 5. | Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | ▨ Ag | ▨ Cd | ▨ In | ▨ Sn | ▨ Sb | Te | I | Xe |
| 6. | Cs | Ba | La• | Hf | Ta | ▨ W | Re | Os | Ir | Pt | Au | ▨ Hg | Tl | ▨ Pb | ▨ Bi | Po | At | Rn |
| 7. | Fr | Ra | Ac•• | | | | | | | | | | | | | | | |
| | | | | ▨ Ce• | Pr | Nd | Pm | Sm | ▨ Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | |
| | | | | Th•• | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Mv | No | | |

Zn as CNS; W as tannin/methyl violet; Ce/Eu as hydroxy-sulphophenylazodiphenyl derivative.

### *Sulphide collectors*

Many sulphides may be used to collect traces of other metals which form insoluble sulphides. The use of cadmium sulphide to collect copper from nickel and lead salts has already been mentioned[34] and it also has been used to gather iron and mercury. Some remarkable examples of high gathering power have been reported for this series as witness the collection of 0.02 μg of mercury from 1 l of solution on copper(II) sulphide[38] and of 1 μg of gold from 1000 l of sea water on lead sulphide[39].

### *Hydrous oxides of aluminium, iron(III) and manganese(IV)*

These are all very efficient gathering agents though their selectivity may appear to be somewhat low at first sight. A few typical examples of their use are cited below to illustrate their sensitivity and range of application.

*Aluminium hydroxide* has been used for the concentration of 1 μg of titanium[40] from 1 l of solution.

*Iron(III) hydroxide* has been applied to the concentration of 0.1 μg of vanadium from 1 l of solution[41] and for the separation of μg amounts of palladium from mg amounts of silver[42].

*Manganese(IV) oxide* may be somewhat more selective than the others. Thus it has been applied to the separation of antimony and thallium in copper and lead salts[43] and also for tin from arsenic and copper[44].

### *Organic reagents*

Many organic reagents have been used such as mandelic acid[45,46], anthranilic acid[47], cupferron[48] and 8-hydroxyquinoline[49]. The behaviour of copper oxinate as a collector is shown in Table X[50].

Lastly, special mention should be made of recent Russian work on methyl violet–iodide as a collecting agent. Metals gathered by this system are shown in Table XI. High selectivity can be obtained for certain metals within the group. Indium for example can be recovered at a dilution level of 1 μg in 20 l selectively in the presence of all the other ions which coprecipitate with this system[51]. This is done by limiting the amount of iodide added when all the other metals coprecipitate without the indium. Subsequently the addition of more iodide and methyl violet to the filtrate brings down the indium. A 20–30-min standing time is required and a 0.5 *M* sulphuric acid medium is used.

Copper can also be coprecipitated selectively within the group[52]. This is done by coprecipitating from a medium containing free iodine. Copper is masked by this procedure and may then be brought down by reducing the iodine in the filtrate through addition of hydroxylamine.

In conclusion it is hoped that these few examples of the concentration of traces of inorganic ions from aqueous solution by the technique of solid phase distribution will serve to focus some attention on its potentialities as an analytical tool. It is probable that systematic examination of the technique, particularly in relation to solvent extraction, may prove that it is at least equally effective and complementary.

## ACKNOWLEDGEMENTS

The author is grateful to the organising committee of the 14th Annual Louisiana State

University Symposium on Analytical Chemistry for the opportunity to present this paper and also wishes to acknowledge his indebtedness to the publications of Sandell[35] and of Morrison and Freiser[29] as valuable sources of information.

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# THE EFFECT OF HEAT ON SOLUTIONS OF CERIUM(IV) SULPHATE IN SULPHURIC ACID AND SOME ANALYTICAL IMPLICATIONS

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(Received February 20th, 1961)

## INTRODUCTION

It is commonly stated[1] that cerium(IV) sulphate solutions are stable when heated. This distinctive feature of cerium(IV) sulphate solutions has resulted in their application in numerous analytical methods involving the use of an excess of reagent at, or near, the boiling point, the residual oxidising agent subsequently being determined by titration with a suitable reagent.

The use of cerium(IV) solutions in analytical chemistry has been reviewed recently by YOUNG[2] and PETZOLD[3]. PETZOLD has summarised the literature on the stability of cerium(IV) solutions and quotes the figures of WILLARD and YOUNG[4]. According to the details given in their 1929 paper, these workers found that samples of 0.1 *N* cerium(IV) sulphate in 0.9 to 1.8 *M* sulphuric acid showed no losses after boiling under reflux for up to 5 h. It is not commonly recognised that in a later paper (1930) WILLARD AND YOUNG, in reporting the reaction of various organic acids with cerium(IV) sulphate in sulphuric acid solution under analytical conditions, mention the need for corrections of "0.03–0.05 ml" to allow for the loss of oxidising agent on boiling. The occurrence of this "blank" in these experiments was attributed to the oxidation being carried out in a beaker, whereas in the previous experiments, in which no blank was detected, a flask and reflux condenser were employed. In the experiments described, involving relatively unreactive organic acids such as formic or acetic acids, losses of cerium(IV) amounting to up to "0.21 ml" were encountered. BERRY[5], who in 1929 investigated the use of boiling cerium(IV) solutions for the quantitative oxidation of tartrates, reported that he had repeated WILLARD AND YOUNG's first set of experiments and confirmed the stability of cerium(IV) sulphate. Solutions of cerium(IV) containing appreciable concentrations of nitrate or perchlorate ions were early shown to lack analytical stability on boiling[4]. SMITH AND SULLIVAN[6] have observed only slight changes (±0.03%) in an approximately 0.1 *N* solution of ceric ammonium nitrate in sulphuric acid, of concentration up to 0.5 *M*, after heating at 100° under a reflux condenser for periods of time as long as 3 h.

In marked contrast to these observations, WEISS AND SIEGER[7] have reported significant losses, of 13 to 20% in 0.1 *N* cerium(IV) sulphate solutions on boiling, the loss being minimised by the addition of silver sulphate. Their experimental details are, however, meagre and it is difficult to appreciate fully the significance of their results. PETZOLD[3] has commented that these results might well have arisen from the presence of traces of material which could act catalytically in reactions involving the loss of cerium(IV) from solution, such as

$$2\ \mathrm{Ce}^{+4} + \mathrm{H_2O} \rightarrow 2\ \mathrm{Ce}^{+3} + 2\ \mathrm{H}^{+} + \tfrac{1}{2}\mathrm{O_2}$$

This latter reaction is thermodynamically possible in acid solution, as is shown by the high value of the redox potential of Ce(IV)/Ce(III) in sulphuric acid ($E_0 = 1.44$ V at 25° in 1 $M$ sulphuric acid), compared with that for the oxidation of water in acid solution, ($2\ \mathrm{H_2O} \rightleftharpoons \mathrm{O_2} + 4\ \mathrm{H}^{+} + 4\ \mathrm{e}$; $E_0 = -1.229$ V at 25°)[8]. The values for the redox potentials of the Ce(IV)/Ce(III) couples in nitric and perchloric acid are higher still, these solutions being appreciably less stable than the sulphuric acid system.

Although it is customary to refer to cerium(IV) solutions in terms of $\mathrm{Ce}^{+4}$, this ion is known not to be present in appreciable amounts, if at all, when ligand groups such as sulphate or nitrate are present; however, there are in these solutions which are only stable in the presence of acid, appreciable amounts of anionic species containing cerium(IV). Only in perchloric acid solution is the $\mathrm{Ce}^{+4}$ ion probably present to any great extent. The crystal structure of certain basic salts obtained from solution shows[9] them to contain poly cations such as $[\mathrm{Ce_6O_4(OH)_4}]^{+12}$. Species of this kind containing several cerium(IV) atoms may be present in the cerium(IV) solutions as employed. Whatever the true nature of the species present, it is to be expected, in general, that the behaviour will be dependent on the acid concentration. Solutions with pH values up to 4 are of particular interest since this range is readily accessible; in the case of solutions of pH approaching 4 a situation of incipient precipitation arises.

In commenting upon the stability of cerium(IV) sulphate solutions, it is relevant to note that ceric oxide reacts with concentrated sulphuric acid on heating with appreciable reduction of the cerium(IV), and that from time to time various ill-defined basic salts containing both cerium(IV) and cerium(III) have been reported to be obtained from sulphuric acid solution of cerium(IV) compounds, often merely on standing; further investigation of these observations is clearly desirable.

## METHODS

Our attention was drawn to the inherent instability of acid ceric sulphate solutions at temperatures above 40° by difficulties encountered in the analysis of certain phosphites by the method of BERNHART[10] in which for the oxidation, an excess of ceric sulphate is used at the boiling point. RAO AND RAO[11] have drawn attention to the inconsistency of the results by this method and have proposed the use of silver(I) ion as catalyst, thus enabling the reactions to be carried out at slightly lower temperatures and with a shorter heating time.

Investigation showed that acidified ceric sulphate solutions underwent loss of oxidation equivalent on heating and that this loss was dependent upon a number of factors. The reaction taking place is reduction of cerium(IV) with resultant oxidation of water, as is shown by the restoration of the cerium(IV) by treatment with sodium bismuthate of the cerium(III) produced. The extent of the loss varied considerably, in general being below about 2% for approximately 0.1 $N$ cerium(IV) sulphate solutions in 1.5 $M$ sulphuric acid, heated for up to 1 h under reflux; values as high as 20% may, however, be encountered for approximately 0.01 $N$ cerium(IV) sulphate solutions. At temperatures below reflux the extent of the reaction is considerably less, being in general below 1%. It is intended to publish an account of these and other experiments later, but it seems of importance at this stage to report such aspects of the work as are relevant to the analytical application of cerium(IV) sulphate solutions.

## EXPERIMENTAL

Experiments were conducted by heating various volumes of cerium(IV) sulphate solutions for varying times under specified conditions and observing the decrease in ferrous ammonium sulphate titre. Solutions were, as far as possible, always titrated under the same conditions, ferroin being employed as indicator. It was established that loss of cerium(IV) occurred even at temperatures as low as 45° and that an appreciable difference in behaviour exists between solutions in which boiling actually occurred, and those in which it did not.

There is a distinction between solutions below and those at the reflux temperature, as regards the extent of the loss quoted earlier, and also the dependence of this extent on the physical conditions of heating. In both, the loss of cerium(IV) occurs in the course of an initial zero order reaction which comes to an abrupt stop after various periods of time up to 30 min. The rate of this initial reaction is much greater at the boiling point than at lower temperatures. The length of time for which it occurs and hence the extent, depends on physical factors, there being a dependence on the solution–glass surface area ratio and type of heating at reflux temperature. At lower temperatures the reaction time depends on the reaction rate, which is probably controlled by the precise surface conditions, faster reactions proceeding for shorter times. The same inverse dependence is found for all temperatures (45–85°) studied below boiling point. As heating is continued, no further loss occurs until, for periods of heating longer than 1 h, some precipitation begins, catalysing further decomposition of the cerium(IV).

Below reflux temperature the rate of the initial reaction is probably dependent on the conditions of the surface of the vessel, the highest rate being achieved on treatment of the surface with boiling 3 *M* sulphuric acid for 25 min before use. Evidence suggests that repeated use of the vessels without this treatment leads to the extent of the loss becoming less. The deactivation of the surface of the vessel, probably by the products of the initial reaction, may lead to a situation where virtually no loss of cerium(IV) occurs on heating. This phenomena might well serve to explain the absence of loss found by other workers. As the vessel walls become catalytically inactive no visible deposit is apparent, although in certain experiments a white solid is sometimes seen. The variation in reaction rate with surface conditions results in wide variations in the extent of the reaction found after heating for a standard time, similar to that accepted as generally useful in quantitative cerium(IV) sulphate oxidations. For example, for a cerium(IV) solution of normality 0.145 *N* and sulphuric acid concentration of 1.5 *M*, after 30 min at 64° the loss varied from 0.03% to 0.3% depending on the pretreatment of the flasks. Variations in acid concentration led to an increase in the loss as the sulphuric acid concentration increased, optimum low values for the loss being at about 1 *M*. Below 0.5 *M* precipitation begins on raising the temperature, the precise acid concentration depending on the cerium(IV) concentration, and decreasing with decreasing cerium(IV) concentration. With this precipitation losses of cerium(IV) increase owing to the catalytic effect of the precipitate. It is possible to redissolve this precipitate by adding sulphuric acid before titration.

Under certain conditions the precipitated material redissolves simply on cooling, although this is in general a slow process. Data on the variation of loss with acid concentration is shown in Table I.

TABLE I

20-ml portions of 0.145 *N* cerium(IV). Time of heating, 65 min. Temperature 87.0° ± 0.1°

| *Overall acid concentration* | % *loss* |
|---|---|
| 10 | 1.70 |
| 4.5 | 0.60 |
| 2.6 | 0.56 |
| 1.1 | 0.40 |
| 0.9 | 0.50 |
| 0.7 | 0.80 |

The effect of temperature is not a simple one, although one can state that below 40° the loss is in general negligible. Variation of loss with ceric solution normality below reflux temperature was not studied.

Experiments at the boiling point were carried out under reflux conditions, the temperature varying mainly with the acid concentration of the solutions studied. As the sulphuric acid concentration increases up to 5 *M*, the temperature gradually increases to 110°; with higher acid concentrations, considerably higher temperatures are attained, cerium(IV) solutions in 50% sulphuric acid refluxing at about 145°.

It became apparent that conditions of boiling (*i.e.* type of heating, extent of bubbling, even the shape of vessel) affected the results very markedly as is shown in Table II, in which variations with vigour of boiling are noted. The terms gentle, moderate and vigorous reflux refer to the rate of formation of bubbles.

TABLE II

VARIATION OF LOSS WITH CONDITIONS OF REFLUX

10 ml of a 0.0113 *N* cerium(IV) solution, overall acid concentration 1.3 *M*

| | % *loss* |
|---|---|
| 10 min under vigorous reflux | 2.7 |
| 10 min under moderate reflux | 1.6 |
| 73 min under vigorous reflux | 7.9 |
| 73 min under moderate reflux | 5.8 |
| 73 min under gentle reflux | 2.5 |

The extent of the loss of cerium(IV) varies widely from experiment to experiment unless care is taken carefully to standardise the conditions, such as the agitation of the solution and the extent of interface between solution, flask and air. The effect of variation in cerium(IV) and acid concentrations, as well as volume of solution is shown in Table III.

If the acid concentration and the experimental conditions are constant the absolute loss of cerium(IV) equivalents tends to be independent of the cerium(IV) concentration. Consequently larger percentage losses are found for more dilute solutions. This follows from the idea that the controlling factor is the catalytic activity of the glass surface which will be independent of the cerium(IV) concentration. The extent of the reaction can be increased by increasing the surface area of glass available, for example by adding Pyrex glass helices. The effect of acid concentration is shown in Table IV.

TABLE III

LOSS OF CERIUM(IV) IN PYREX GLASS VESSEL

| *Cerium(IV) concentration, N* | *$H_2SO_4$ concentration, M* | *Volume of solution ml* | *% loss Cerium(IV) during initial reaction* |
|---|---|---|---|
| 0.1191 | 2.4 | 25 | 1.34 |
| 0.0475 | 2.7 | 25 | 2.52 |
| 0.0835 | 1.5 | 10 | 4.19 |
| 0.0305 | 2.6 | 35 | 2.26 |
| 0.0762 | 2.6 | 35 | 0.68 |
| 0.0153 | 2.6 | 35 | 3.18 |
| 0.0414 | 2.2 | 35 | 1.24 |
| 0.0494 | 1.4 | 25 | 1.05 |

TABLE IV

VARIATION OF LOSS WITH ACID CONCENTRATION

*(a) Samples of 20 ml 0.0056 N cerium(IV) sulphate heated under reflux for 40 min*

| *Concentration of $H_2SO_4$ M* | *% loss* |
|---|---|
| 0.13 | 10.76 |
| 0.58 | 7.91 |
| 1.0 | 7.74 |
| 2.8 | 7.94 |
| 4.6 | 8.42 |
| 9.1 | 13.53 |

*(b) Samples of 50 ml 0.050 N cerium(IV) sulphate heated under reflux for 56 min*

| *Concentration of $H_2SO_4$ M* | *% loss* |
|---|---|
| 0.8 | 2.01 |
| 1.5 | 1.41 |
| 2.6 | 1.77 |
| 4.4 | 1.89 |
| 6.2 | 2.57 |
| 9.8 | 4.58 |

PETZOLD[3] suggested that the erratic results of WEISS AND SIEGER[7] were due to catalysis of the cerium(IV)–water reaction by impurities. We have examined this point by using a solution of ceric sulphate prepared from spectroscopically pure cerium(IV) oxide and AnalaR reagent sulphuric acid, and we can find no difference in behaviour, as far as loss of oxidation equivalent on heating is concerned, between this solution and solutions prepared from commercial ceria or commercial ceric sulphate and commercial sulphuric acid.

The effect of added silver(I), copper(II), and mercury(II) ions on the loss of cerium(IV) varies with the concentration of the ions; in general the extent of the loss on heating is increased. A decrease in the extent is, however, found for copper(II) when the concentration of copper(II) present is less than $4 \cdot 10^{-3}$ *M*. Larger concentrations increase the loss again. A careful study of reactions involving phosphite shows that here, although the loss is not eliminated, it may be substantially reduced.

The loss of oxidation equivalent in cerium(IV) solution is of obvious importance in analytical reactions which require a temperature much above room temperature. For reactions at reflux temperature the method of heating is important in view of the variability of the loss with the nature of the bubbling, etc. With this in mind the wide variations found by WEISS AND SIEGER[7] can be largely attributed to their method of heating, apparently on sand baths. RAO AND RAO[11] found it necessary to employ a boiling water bath in order to control the errors encountered in the oxidation of the phosphite by cerium(IV).

Two points emerge from this work. Firstly, the loss of oxidation equivalent varies widely depending very much on the conditions of the reaction. Secondly, it is not possible to evaluate in advance the effect of the various factors and consequently, when the reagent is employed in analytical reactions, care must be taken to investigate the magnitude of the blank carefully.

The evidence so far collected is indicative of a reaction between the cerium(IV) species and the water leading to the formation of hydroxyl radicals, which subsequently break down probably to gaseous oxygen. The reaction is apparently surface catalysed and diffusion to the surface of the glass and the nature of this surface are clearly important factors in determining the rate of the reaction, although there is little evidence to suggest that the extent of the initial fast reaction is related in a simple fashion to the catalytic activity of the surface. The effect of the metal ions is to catalyse homogeneously the reaction of cerium(IV) and water, and thus increase the loss. Phosphite on the other hand will minimise the loss by reacting with the hydroxyl radicals almost as soon as they are formed at the surface of the vessel, thereby reducing the probability of the radicals reacting to give oxygen. We have found that phosphite complexes with cerium(IV) in sulphuric acid solution and that the oxidation of phosphite in these solutions, on heating, proceeds probably by way of reaction of phosphite ions with hydroxyl radicals. The incipiently formed radicals will thus be liable to interact with phosphite rather than to escape to the solution.

TABLE V

THE CERIMETRIC ANALYSIS OF PHOSPHITE[10] BY OXIDATION OF $SrH_2(HPO_3)_2$

(Theoretical equivalent weight 62.3)

| *Volume of a solution containing 1.859 g $SrH_2(HPO_3)_2$/100 ml* | *ml 0.1191 Cerium(IV) reacted* | *Apparent equivalent weight* |
|---|---|---|
| 0.2 | 0.94 | 33.4 |
| 0.5 | 1.64 | 47.9 |
| 1.0 | 2.82 | 55.7 |
| 2.0 | 5.19 | 60.5 |
| 5.0 | 12.57 | 62.4 |
| 10.0 | 24.25 | 64.7 |

Each solution had an initial cerium(IV) conc. of 0.0487 *N*, $H_2SO_4$ conc. 2 *M* and Ag(I) conc. (*cf.* ref.[11]) $6.1 \cdot 10^{-3}$ *M*.

On extrapolation of a plot of the ml cerium(IV) solution reacted against the amount of phosphite present to zero phosphite, a "blank" loss of cerium(IV) of 0.47 ml solution is found. This may be used to work out a corrected equivalent weight, a value of 64 being obtained from the gradient of the plot. If the equivalent weight (apparent) is plotted against the quantity of phosphite taken a plateau value is found near the theoretical equivalent at 62.3.

In the analysis of phosphites it has been found necessary to adopt a procedure whereby the oxidation equivalent is determined for different amounts of phosphite using a constant amount of ceric sulphate solution in sulphuric acid and the resulting data is then plotted to enable the loss of cerium(IV) to be evaluated (Table V). The appearance of solid material in the solution may make the loss considerably larger and the accurate assessment of the correction difficult.

## CONCLUSION

It must be admitted that the work described above, whilst revealing the possibilities of serious errors in determinations based on the use of ceric sulphate solutions, does not offer any single solution to the problem, which must be treated and solved independently in every situation. Previous difficulties reported in certain applications of cerium(IV) sulphate solutions by other workers, now can be recognised as arising from the losses described above.

## ACKNOWLEDGEMENT

We thank Messrs. Albright and Wilson for a grant to D.G.

## SUMMARY

Ceric sulphate solutions may undergo appreciable losses of cerium(IV) on heating. The overall loss is acid dependent, being at a minimum in about 1 *M* sulphuric acid, and is almost independent of the cerium(IV) concentration. Consequently as the concentration falls the actual percentage loss increases. The loss, resulting from the reaction of cerium(IV) with water, is catalysed heterogeneously at the glass surface and also on the surface of any precipitated material. The extent of the loss varies considerably with the conditions of the experiment. Solutions of ceric sulphate prepared from commercial grade cerium(IV) sulphate or ceria and from spectroscopically pure ceria, behave in the same fashion. The effect of added silver(I), copper(II), mercury(II) and phosphite ions in the cerium(IV)–water reaction is reported.

## RÉSUMÉ

Les auteurs ont effectué une étude démontrant que les pertes en cérium(IV), par chauffage de solutions de sulfate de cérium, dépendent principalement de la teneur en acide. La perte est minimum dans l'acide sulfurique 1 *M* et ne dépend pratiquement pas de la concentration en cérium(IV).

## ZUSAMMENFASSUNG

Es wird nachgewiesen, dass der Verlust an Ce(IV) beim Erhitzen einer Ce(IV)-sulfatlösung vom Säuregehalt der Lösung abhängt. Der Verlust ist am geringsten in einer 1 *M* Schwefelsäurelösung und ist unabhängig von der Ce-Konzentration.

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# EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

## II. DETERMINATION OF COPPER, NICKEL, IRON, CHROMIUM AND VANADIUM

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(Received February 15th, 1961)

### INTRODUCTION

An extractive method of end-point detection has been applied to the titrimetric determination of cobalt with EDTA[1]. The cobalt was determined by the addition of an excess but known volume of standard EDTA solution, and back-titration with a standard cobalt solution. The end-point was indicated by the appearance, in the chloroform layer, of the blue colour of the ion-association pair triphenylmethylarsonium tetrathiocyanato cobaltate(II).

In the present paper, this method has been extended to the determination of the metals copper, nickel, iron, chromium and vanadium which, like cobalt, form coloured EDTA complexes. The extractive method possesses advantages, as described in the first paper[1]; these advantages are particularly significant in the case of chromium.

Copper, nickel and iron have been determined by the back-titration of excess EDTA with standard cobalt solution using thiocyanate as indicator, the titration being carried out in a 1 : 1 acetone–water mixture[2]. Ether has been used to assist the observation of the end-point in the titration of iron(III) with EDTA using thiocyanate as indicator[3,4]. Chromium(III) and vanadium(IV) have been determined by the back-titration of excess EDTA with various metal solutions, using appropriate indicators; for example, manganous sulphate with Eriochrome Black T indicator[5].

### APPARATUS AND REAGENTS

The flask used for the titrations has already been described[1].

*Solutions used*

(A.R. quality reagents were used wherever possible).

*Standard EDTA solution*. A 0.01 *M* solution of the disodium salt. This solution was standardised against zinc solution using Eriochrome Black T as indicator.

*Standard cobalt(II) solution*. A 0.01 *M* solution of iron-free cobalt ammonium sulphate.

*Buffer solutions*. (*a*) pH = 9.3. Concentrated ($d = 0.880$) aqueous ammonia (150 ml) and ammonium chloride (160 g) made up to 1 l with water. (*b*) pH = 8.5. Concentrated ($d = 0.880$) aqueous ammonia (50 ml) and ammonium chloride (215 g) made up to 1 l with water.

Ammonia, approx. 1 *M*. Potassium thiocyanate (50%). Triphenylmethylarsonium chloride (1%).

Solutions were prepared using distilled water which had been passed through a column containing cation exchange resin in the sodium form. Polythene containers were used for storage.

### PROCEDURE

The sample metal ion solution (nickel(II), copper(II), iron(III), chromium(III) or vanadium(IV)) and 25 ml of standard EDTA solution (50 ml for chromium) are pipetted into the titration flask. The sample solution should contain from 2 to 12 mg of nickel or copper, or from 2 to 10 mg of iron, chromium or vanadium*. (If chromium is being estimated, the acid solution must be boiled for at least 5 min after the addition of EDTA to ensure complete complex formation). If necessary, ammonia is added until litmus paper just turns blue. Approximately 10 ml of chloroform are then added, followed by 2 ml of the appropriate buffer solution, 5 ml of potassium thiocyanate solution and 3 ml of triphenylmethylarsonium chloride solution. Buffer solution (*a*) (pH = 9.3) is used for nickel and copper, and solution (*b*) (pH = 8.5) for iron, chromium and vanadium. The excess EDTA is then back-titrated using standard cobalt solution as titrant. The cobalt solution should be added dropwise as the end-point is approached, the flask being stoppered and shaken after the addition of each drop. The end-point is indicated by the appearance of a blue colour in the chloroform layer.

### RESULTS

The metal content of different volumes of a solution of known concentration was determined for each of the metals (Tables I to V). With the exception of the first group of results in Table I, which were obtained by determining a smaller quantity

TABLE I

| *mg of Ni added* | *mg of Ni found* | *% Deviation from Ni added* | *Mean mg of Ni found* | *% Deviation of mean from Ni added* | *Maximum % deviation of Ni found from mean* |
|---|---|---|---|---|---|
| 1.256 | 1.294 | +3.0 | 1.277 | +1.7 | 1.3 |
| 1.256 | 1.287 | +2.5 | | | |
| 1.256 | 1.269 | +1.0 | | | |
| 1.256 | 1.263 | +0.6 | | | |
| 1.256 | 1.269 | +1.0 | | | |
| 3.141 | 3.149 | +0.3 | 3.151 | +0.3 | 0.5 |
| 3.141 | 3.137 | −0.1 | | | |
| 3.141 | 3.143 | +(<0.1) | | | |
| 3.141 | 3.161 | +0.6 | | | |
| 3.141 | 3.167 | +0.8 | | | |
| 6.281 | 6.298 | +0.3 | 6.291 | +0.2 | 0.3 |
| 6.281 | 6.280 | −(<0.1) | | | |
| 6.281 | 6.274 | −0.1 | | | |
| 6.281 | 6.298 | +0.3 | | | |
| 6.281 | 6.304 | +0.4 | | | |

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* For the estimation of greater quantities of the metals than those quoted, more EDTA solution should be added, or the concentrations of both EDTA and the standard cobalt solution should be increased. The sample volume should not be more than 150 ml for the quantities of buffer, potassium thiocyanate and triphenylmethylarsonium chloride specified. For larger sample volumes, more of these reagents should be used.

of nickel than that recommended in the procedure, it can be seen that the mean value of metal determined may normally be expected to be within 0.5% of the true value, while the maximum variation about this mean is also of the same order, thus leading to a maximum expected error of about 1% for any single determination. One observes in fact that, neglecting the first group of nickel results, the error exceeds 1% in only two of the seventy estimations.

TABLE II

| *mg of Cu added* | *mg of Cu found* | *% Deviation from Cu added* | *Mean mg of Cu found* | *% Deviation of mean from Cu added* | *Maximum % deviation of Cu found from mean* |
|---|---|---|---|---|---|
| 3.211 | 3.188 | −0.7 | 3.183 | −0.9 | 0.6 |
| 3.211 | 3.201 | −0.3 | | | |
| 3.211 | 3.175 | −1.1 | | | |
| 3.211 | 3.182 | −0.9 | | | |
| 3.211 | 3.169 | −1.3 | | | |
| 6.421 | 6.422 | +(<0.1) | 6.409 | −0.2 | 0.2 |
| 6.421 | 6.396 | −0.4 | | | |
| 6.421 | 6.409 | −0.2 | | | |
| 6.421 | 6.396 | −0.4 | | | |
| 6.421 | 6.422 | +(<0.1) | | | |
| 12.84 | 12.79 | −0.4 | 12.78 | −0.5 | 0.1 |
| 12.84 | 12.79 | −0.4 | | | |
| 12.84 | 12.78 | −0.5 | | | |
| 12.84 | 12.79 | −0.4 | | | |
| 12.84 | 12.77 | −0.5 | | | |

TABLE III

| *mg of Fe added* | *mg of Fe found* | *% Deviation from Fe added* | *Mean mg of Fe found* | *% Deviation of mean from Fe added* | *Maximum % deviation of Fe found from mean* |
|---|---|---|---|---|---|
| 2.835 | 2.853 | +0.6 | 2.848 | +0.5 | 0.6 |
| 2.835 | 2.841 | +0.2 | | | |
| 2.835 | 2.836 | +(<0.1) | | | |
| 2.835 | 2.864 | +1.0 | | | |
| 2.835 | 2.847 | +0.4 | | | |
| 5.669 | 5.712 | +0.8 | 5.699 | +0.5 | 0.5 |
| 5.669 | 5.712 | +0.8 | | | |
| 5.669 | 5.689 | +0.4 | | | |
| 5.669 | 5.712 | +0.8 | | | |
| 5.669 | 5.671 | +(<0.1) | | | |
| 11.34 | 11.40 | +0.5 | 11.38 | +0.4 | 0.2 |
| 11.34 | 11.37 | +0.3 | | | |
| 11.34 | 11.37 | +0.3 | | | |
| 11.34 | 11.40 | +0.5 | | | |
| 11.34 | 11.38 | +0.4 | | | |

## DISCUSSION

The suggested pH at which the titration is to be commenced is 9.3 in the case of nickel and copper, and 8.5 for iron, chromium and vanadium. It was found that the solution

TABLE IV

| *mg of Cr added* | *mg of Cr found* | *% Deviation from Cr added* | *Mean mg of Cr found* | *% Deviation of mean from Cr added* | *Maximum % deviation of Cr found from mean* |
|---|---|---|---|---|---|
| 2.593 | 2.609 | +0.6 | 2.597 | +0.2 | 0.5 |
| 2.593 | 2.599 | +0.2 | | | |
| 2.593 | 2.588 | −0.2 | | | |
| 2.593 | 2.604 | +0.4 | | | |
| 2.593 | 2.583 | −0.4 | | | |
| 5.186 | 5.234 | +0.9 | 5.217 | +0.6 | 0.5 |
| 5.186 | 5.218 | +0.6 | | | |
| 5.186 | 5.192 | +0.1 | | | |
| 5.186 | 5.228 | +0.8 | | | |
| 5.186 | 5.213 | +0.5 | | | |
| 10.37 | 10.43 | +0.6 | 10.41 | +0.4 | 0.3 |
| 10.37 | 10.41 | +0.4 | | | |
| 10.37 | 10.38 | +0.1 | | | |
| 10.37 | 10.44 | +0.7 | | | |
| 10.37 | 10.39 | +0.2 | | | |

TABLE V

| *mg of V added* | *mg of V found* | *% Deviation from V added* | *Mean mg of V found* | *% Deviation of mean from V added* | *Maximum % deviation of V found from mean* |
|---|---|---|---|---|---|
| 2.550 | 2.551 | +(<0.1) | 2.545 | −0.2 | 0.4 |
| 2.550 | 2.546 | −0.2 | | | |
| 2.550 | 2.546 | −0.2 | | | |
| 2.550 | 2.536 | −0.5 | | | |
| 2.550 | 2.546 | −0.2 | | | |
| 5.099 | 5.101 | +(<0.1) | 5.111 | +0.2 | 0.2 |
| 5.099 | 5.112 | +0.3 | | | |
| 5.099 | 5.117 | +0.4 | | | |
| 5.099 | 5.117 | +0.4 | | | |
| 5.099 | 5.107 | +0.2 | | | |
| 10.20 | 10.22 | +0.2 | 10.20 | 0.0 | 0.2 |
| 10.20 | 10.20 | 0.0 | | | |
| 10.20 | 10.21 | +0.1 | | | |
| 10.20 | 10.19 | −0.1 | | | |
| 10.20 | 10.19 | −0.1 | | | |

could be at least 0.5 pH units above or 1.0 pH unit below these values without affecting the results. The pH variations which could be encountered in practice would be well within this range.

The range of volumes of potassium thiocyanate, triphenylmethylarsonium chloride and buffer solutions giving a titration deviating by no more than 0.1 ml from the normal result have been found for the cobalt determination[1]. These volumes (KSCN, 1 to 30 ml; $Ph_3MeAsCl$, 1 to 30 ml; and buffer, 0.5 to 8 ml) again gave an error no greater than 0.1 ml in the titrations involved in the present metal determinations with one exception only. This occurred in the case of copper(II), where 8 ml of buffer solution gave a high titration result; however, reduction to 7 ml reduced the titration error to 0.1 ml. This effect may be attributed to the ammonia in high concentration competing with the EDTA as a complexing agent for the copper.

After the addition of excess EDTA to the metal solution, the resulting solution should, if necessary, be first neutralised with ammonia. The chloroform and other reagents may then be added in any order without affecting the result of the titration. Ammonia, if added before the EDTA, may interfere with the determination by precipitating the metal hydroxide. Again, if thiocyanate is added before the EDTA to the copper(II) solution, partial reduction to copper(I) occurs, thus giving a low result for the copper determination.

When quantities of chromium near the upper limit of the specified range (10 mg) were determined, 25 ml of EDTA provided an insufficient excess, for even after boiling the solution for 20 min all of the chromium was not complexed. Accordingly, 50 ml of EDTA has been recommended in the procedure for chromium.

For the determination of quantities of metals of the order of ten times those specified in the procedure, 0.1 $M$ solutions of cobalt and EDTA may be used and very sharp end-points are still obtained, provided that more buffer is used. On the other hand, if one attempts to determine similar quantities of the metals with 0.1 $M$ solutions by ordinary methods (for nickel and copper, direct titration with EDTA using murexide as indicator; for iron, direct titration using Variamine Blue indicator; for chromium and vanadium, back-titration with standard zinc solution using Eriochrome Black T as indicator) comparable results are obtained for nickel, copper and iron, but in the case of vanadium the end-point is very diffuse, and with chromium, the end-point can not be seen at all, due to the intensity of colour of the solution. Hence, it may be seen that the extractive end-point method is more widely applicable to coloured solutions than methods in which the end-point is observed in the aqueous phase.

## SUMMARY

A method for the determination of nickel, copper, iron, chromium and vanadium by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending on the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the determination of these metals in highly coloured aqueous solutions. The maximum expected error is of the order of 1%, and in the majority of determinations the error is 0.5% or less.

## RÉSUMÉ

Une méthode est proposée pour le dosage du nickel, du cuivre, du fer, du chrome et du vanadium par addition d'EDTA en excès et titrage en retour au moyen d'une solution étalon de cobalt. La détection du point final se fait par extraction dans le chloroforme du composé bleu $[Ph_3MeAs]_2[Co(SCN)_4]$, permettant ainsi un dosage même dans des solutions fortement colorées.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Nickel, Kupfer, Eisen, Chrom und Vanadium. Die Lösung wird mit Chloroform, einem Überschuss von EDTA, Kaliumthiocyanat und Triphenylarsoniumchlorid versetzt und der Überschuss an EDTA mit einer Kobaltlösung zurücktitriert. Der Endpunkt wird durch das Auftreten der blauen Farbe des $[Ph_3MeAs]_2[Co(SCN)_4]$ in der Chloroformschicht angezeigt.

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# DOSAGE OXYDIMÉTRIQUE DE L'ACIDE URIQUE PAR L'IODATE ET LE PERIODATE DE POTASSIUM

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(Reçu le 27 février 1961)

On a proposé pour le dosage volumétrique de l'acide urique toute une série d'agents oxydants qui permettent de le déterminer par titrage direct ou par rétitration de l'agent en excès. On utilise notamment des solutions étalons d'iode[1-3], de permanganate de potassium[4], de sulfate de cérium[5], de chloramine T[6], de vanadate de sodium[7], de bromate de potassium en présence d'un bromure[3], de ferricyanure alcalin[8] ou le réactif de Fehling[9].

Nous avons étudié l'oxydation de l'acide urique par l'iodate et le periodate et constaté que la réaction avec ces réactifs s'effectue, dans les solutions convenablement acidifiés par l'acide chlorhydrique, si rapidement, que l'on peut l'utiliser pour un dosage potentiométrique direct. La concentration de l'acide chlorhydrique a une influence non seulement sur la vitesse, mais encore sur l'évolution stoichiométrique de la réaction.

## PARTIE EXPÉRIMENTALE

### *Réactifs*

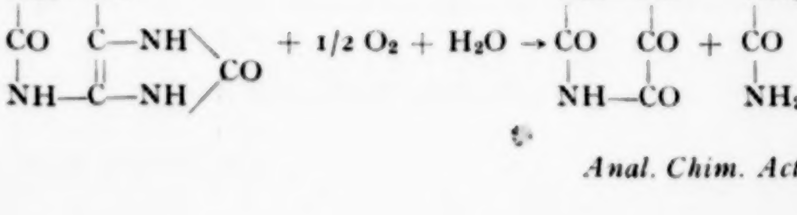
La solution d'acide urique est préparée par dissolution de 1.68 g de produit pur dans 200 ml d'eau distillée bouillante, contenant 1 g de carbonate de lithium, et complétée à un volume de 1000 ml par de l'eau distillée. Le titre a été contrôlé chaque jour par iodométrie[3]. Solution de iodate de potassium (p.a. Merck) 0.01 *M*. Solution de periodate de potassium (purrum Lachema) 0.01 *M*, titreé avec du sulfate d'hydrazine[10].

### *Appareils*

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre EK/21 (Kovodružba, Praha) en utilisant un fil de platine comme électrode indicatrice et une électrode au calomel comme électrode de référence. Le liquide était agité par un dispositif électromagnétique. Les titrages ont été effectués à l'aide d'une microburette de 5 ml (graduées en 0.01 ml).

## RÉSULTATS

Par la plupart des agents, l'acide urique est oxydé (en milieu acide) en formant l'alloxane et l'urée, d'après l'équation:



(1)

La réduction de l'iodate et du periodate dans les solutions chlorhydriques s'effectue en fonction de la concentration de l'acide chlorhydrique et selon la nature de l'oxydant d'après le schéma.

$$IO_3^- + 6\,H^+ + 6\,e \rightarrow I^- + 3\,H_2O \qquad (2a)$$

$$IO_4^- + 8\,H^+ + 8\,e \rightarrow I^- + 4\,H_2O \qquad (2b)$$

$$2\,IO_3^- + 12\,H^+ + 10\,e \rightarrow I_2 + 6\,H_2O \qquad (3a)$$

$$2\,IO_4^- + 16\,H^+ + 14\,e \rightarrow I_2 + 8\,H_2O \qquad (3b)$$

$$IO_3^- + 6\,H^+ + 4\,e \rightarrow I^+ + 3\,H_2O \qquad (4a)$$

$$IO_4^- + 8\,H^+ + 6\,e \rightarrow I^+ + 4\,H_2O \qquad (4b)$$

Pour cette raison nous avons étudié, par titrage potentiométrique direct, l'influence de la concentration de l'acide sur l'évolution stoichiométrique de la réaction de l'acide urique avec l'iodate et avec le periodate.

*Titrage de l'acide urique par l'iodate de potassium*

Au cours de ces expériences nous avons titré, dans des solutions différemment acidifiées par l'acide chlorhydrique, 15 mg d'acide urique par une solution d'iodate de potassium 0.01 *M* dans un volume initial de 50 ml. Nous avons constaté, que dans les solutions contenant 0.4–1.5% de HCl l'oxydation de l'acide urique s'effectue d'après l'éqn. (1), et l'iodate est réduit quantitativement en iode élémentaire (3a). Sur la courbe potentiométrique l'achèvement de la réaction est marqué par une variation brusque du potentiel (voir Fig. 1, courbe A). Les solutions, initialement blanc trouble par la présence de l'acide urique, se clarifient au cours du titrage et se colorent par l'iode. Au voisinage de l'équivalence, il est nécessaire d'attendre 2 min pour que le potentiel se stabilise. L'équivalence étant atteinte, le réactif en excès oxyde l'iode en chlorure de iode. La couleur du iode disparaît, sans que le potentiel change visiblement.

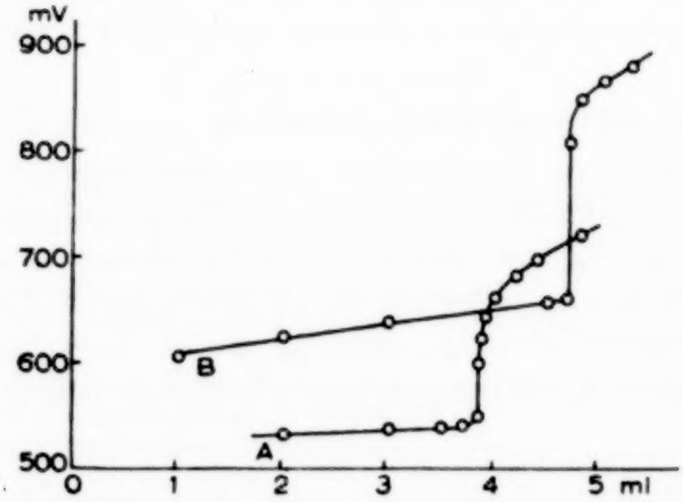


Fig. 1. Titrage de 15 mg d'acide urique par l'iodate de potassium, (A) dans un milieu de HCl à 0.8% (réduction en $I_2$), (B) dans un milieu de HCl à 15% (réduction en ICl).

Dans les solutions neutres ou très peu acidifiées par HCl, la réaction de l'acide urique avec l'iodate ne s'effectuait pas assez rapidement pour qu'on puisse la suivre par titrage potentiométrique. En diminuant la concentration de l'acide chlorhydrique au-dessous de 1.5%, la variation du potentiel correspondant à la réduction de l'iodate en iode devenait de moins en moins nette jusqu'à sa disparition complète.

Une réduction quantitative et immédiate de l'oxydant en chlorure de iode (éqn. 4a) s'effectue au cours du titrage de l'acide urique (éqn. 1) dans les solutions d'acide chlorhydrique à 11–30%. La variation du potentiel au point équivalent est encore plus nette (Fig. 1, courbe B) que dans le cas de la réduction de l'iodate en iode. Le titrage peut être effectué même avec une concentration de HCl plus grande, mais il est nécessaire alors d'attendre un certain temps la stabilisation du potentiel au voisinage du point équivalent. Quand la concentration de l'acide chlorhydrique est inférieure à 11% les résultats dépendent de la vitesse du titrage et ils comportent une erreur positive.

Pour le dosage de l'acide urique il est donc possible d'utiliser le milieu HCl soit à 0.4–1.5% soit à 11–30%. Nous avons déterminé de cette manière de 8–60 mg d'acide urique dans un volume de 50 ml. La différence relative moyenne, calculée chaque fois d'après 10 dosages, était dans le premier cas de 0.14% et dans le deuxième de 0.11%. La variation du potentiel sur 0.02 ml d'oxydant 0.01 $M$ est dans HCl à 0.8% de 50 mV, dans HCl à 15% de 150 mV. Le potentiel au point d'inflexion est aux environs de 580 mV dans le premier milieu et 740 mV dans le second. 1 ml de $KIO_3$ 0.01 $M$ correspond resp. à 4.20275 et 3.3622 mg d'acide urique.

La stabilisation immédiate du potentiel et l'importance de sa variation au point équivalent amènent à recommander à des fins analytiques le milieu HCl à 11–30%.

### *Titrage de l'acide urique par le periodate de potassium*

Afin de voir si le periodate de potassium (dont nous avons étudié précédemment l'utilisation en analyse volumétrique[11]) réagit avec l'acide urique de la même manière que l'iodate, nous avons effectué avec ce réactif les mêmes essais qu'avec l'iodate.

Nous avons constaté que la réduction du periodate en chlorure d'iode (éqn. 4b) s'effectue quantitativement avec la même vitesse et dans les mêmes conditions qu'avec l'iodate. Pendant le titrage potentiométrique de l'acide urique en solution

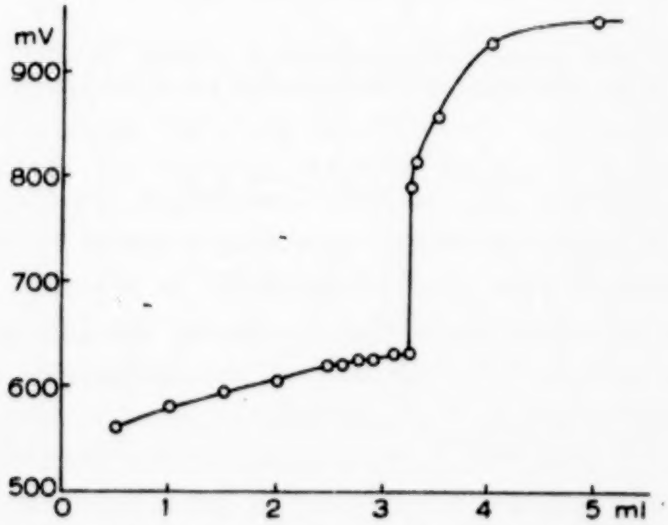


Fig. 2. Titrage de 15 mg d'acide urique par le periodate de potassium dans un milieu de HCl à 15%.

HCl à 11–30% (voir Fig. 2), le potentiel (pendant tout le titrage) se stabilise immédiatement; au point équivalent la variation du potentiel est de 160 mV sur 0.02 ml d'oxydant 0.01 *M*, le potentiel au point d'inflexion est aux environs de 720 mV (en HCl à 15 %). En dosant de 8 à 60 mg d'acide urique la différence relative moyenne (calculée sur dix mesures) était de 0.12%. 1 ml de $KIO_4$ 0.01 *M* correspond à 5.0433 mg d'acide urique.

Le titrage direct de l'acide urique dans les solutions de HCl de concentration inférieure ne conduisait jamais (contrairement au cas de l'iodate) à la réduction du periodate en iode. La présence d'iode élémentaire a pu être qualitativement mise en évidence seulement après une action prolongée du réactif en excès.

## RÉSUMÉ

Il est possible de doser l'acide urique par un titrage potentiométrique direct au moyen d'une solution d' iodate ou de periodate de potassium, dans des solutions acidifiées de manière appropriée par l'acide chlorhydrique. Selon la concentration de HCl le réactif est réduit en chlorure d' iode, ou en iode élémentaire (dans le cas de l'iodate).

## SUMMARY

Uric acid is determined by potentiometric titration with potassium iodate or periodate in solutions containing hydrochloric acid. Depending on the acid concentration the reagent is reduced to iodine monochloride, or to elementary iodine (in the case of iodate).

## ZUSAMMENFASSUNG

Harnsäure kann durch potentiometrische Titration mit Kalium-Jodat oder -Perjodat in Lösungen, die mit Chlorwasserstoffsäure geeignet angesäuert sind, bestimmt werden. Der Konzentration der Chlorwasserstoffsäure entsprechend wird das Reagens zu Jodmonochlorid, bzw. zu elementarem Jod (im Falle von Jodat) reduziert.

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# APPLICATION OF SELENIUM SALTS IN INORGANIC ANALYSIS

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(Received February 5th, 1961)

Several papers[1,2] have appeared from this laboratory dealing with the application of thio salts in qualitative and quantitative analysis. In view of the strong similarity of selenium to sulphur and the analogous reactions of their salts, the behaviour of the selenium salts has now been investigated for the determination of several metals. A general study of the metals which form insoluble sulphides showed that the selenium compounds behave almost exactly like the corresponding sulphur compounds. Those which form thio salts also form soluble seleno salts with excess of sodium selenide and these are decomposed by excess of acid with the complete precipitation of the corresponding selenides. In other cases insoluble selenides are directly precipitated like the sulphides. The main differences between the compounds of sulphur and selenium lie in the greater toxicity of hydrogen selenide and in the greater contamination of the selenide precipitates with the selenium formed by atmospheric oxidation of sodium selenide. If sodium sulphide is prepared below 5° and precipitation is carried out in ice-cold solutions, the oxidation of sodium sulphide with precipitation of sulphur is negligible. But although the oxidation of sodium selenide is reduced at a low temperature, considerable quantities of selenium are still found in the selenide precipitates. Hydrogen selenide is a colourless gas which produces dryness and a pungent and painful sensation on coming in contact with mucous membranes; its smell is similar to hydrogen sulphide. A specially devised apparatus of the type shown below is therefore necessary.

For sodium selenide to be useful for the determination of metals, atmospheric oxidation of sodium selenide must be prevented both in the preparation of the reagent and during its use as a precipitant. Acceptable results can be obtained by maintaining an atmosphere of carbon dioxide or nitrogen in the bottles in which sodium selenide is prepared and the metallic selenides are precipitated provided that care is taken to prevent sodium selenide coming in contact with air. The slightest exposure to air results in contamination with selenium, but this can be removed by washing with carbon disulphide. The precipitated selenide which remains behind can be weighed in a pure form after washing with alcohol and ether successively and drying in a vacuum desiccator.

As an example of what happens when metals are determined as selenides by adopting ordinary precautions to prevent oxidation, arsenic was precipitated as the selenide ($As_2Se_5$); a positive error of 0.3–0.4% was obtained when 20–45 mg of arsenic was precipitated.

The prevention of oxidation by ordinary methods requires extreme care, hence it was considered desirable to devise an apparatus (Fig. 1) in which (*a*) the whole procedure could be carried out without contact with air, (*b*) the hydrogen selenide formed could be removed without contaminating the surrounding atmosphere and (*c*) the temperature of the solutions could be maintained between 5–10°.

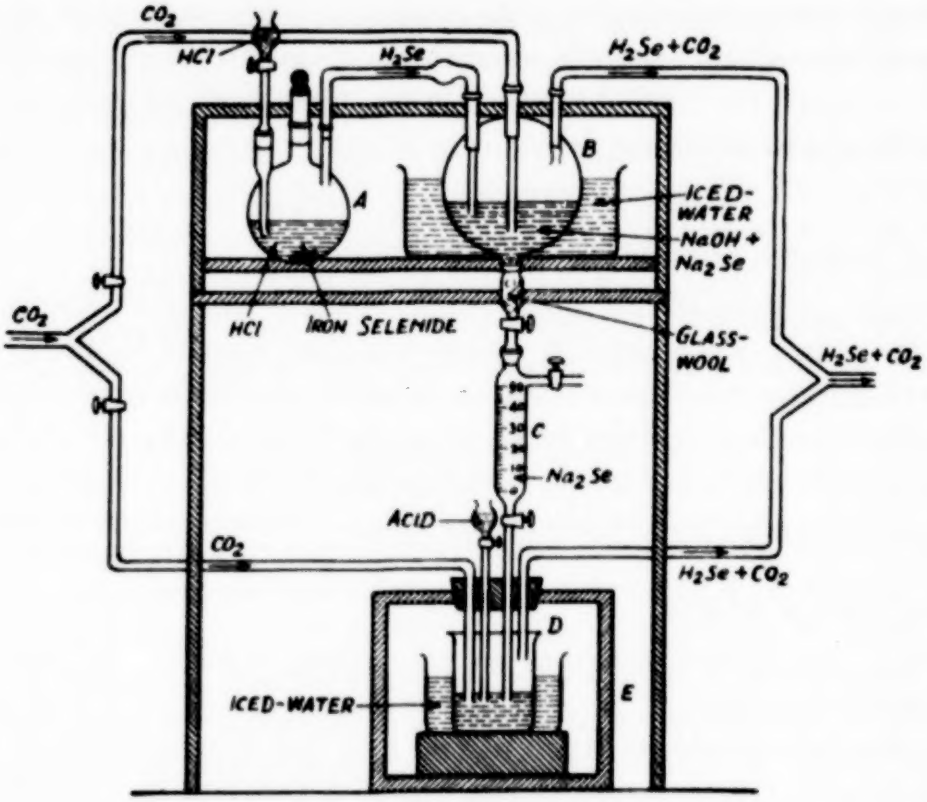

Fig. 1. Apparatus for precipitating selenides.

The following points should be noted with regard to the determination of metals as selenides:

(*1*) The selenides are precipitated by the addition of excess of acid to seleno salts without the heating which is necessary for sulphides.

(*2*) Filtration of the selenides is easier than that of sulphides.

(*3*) All selenides can be weighed after washing with distilled water, alcohol and ether successively and drying in a vacuum desiccator; no heating has been found necessary so far.

It can be seen, therefore, that the selenides provide a more convenient and quicker method of determining metals than sulphides.

Obviously, the apparatus described can be employed for the quantitative precipitation of any metal where oxidation by air interferes.

## EXPERIMENTAL

### *Apparatus* (see Fig. 1)

Hydrogen selenide is generated in flask A by adding concentrated hydrochloric acid to ferrous selenide and is passed into the sodium hydroxide solution in flask B, which is maintained at 5–10° by placing it in iced water. Flask B is fitted with three tubes: the first to remove air in the flask by passing carbon dioxide, the second to conduct hydrogen selenide from flask A, and the third to remove the excess of hydrogen selenide by means of a long rubber tube which leads out of the laboratory.

The sodium selenide solution is placed in burette C and a measured volume is then added to the beaker D containing the cold metallic salt solution. The beaker is placed in a trough containing iced water within a cabinet E which is also fitted with (*1*) a thistle funnel for adding measured quantities of acid, (*2*) a tube for conducting carbon dioxide into the beaker (which removes air from the cabinet and stirs the solution) and (*3*) a tube for removing the hydrogen selenide formed by the addition of acid to the seleno salts. The whole operation is thus carried out easily without any contact with air until the insoluble selenide has been precipitated and is ready for filtration, washing and weighing.

## METHODS

### *Preparation of hydrogen selenide*

Alternate layers of iron filings (obtained by drilling soft iron) and powdered selenium were placed in a Rose crucible which was then heated to 500–650° for about an hour. The resulting cooled mass of ferrous selenide was removed and powdered and a portion was placed in flask A, from which all air had been displaced by carbon dioxide. On adding concentrated hydrochloric acid through the thistle funnel a steady stream of hydrogen selenide was evolved after a few minutes and conducted into flask B.

### *Preparation of sodium selenide*

After flask B had been freed from air by carbon dioxide, 150–200 ml of a 2 *N* sodium hydroxide solution (E. Merck) was introduced and cooled to a temperature of 5–10°. Hydrogen selenide was then passed into this solution for 5–7 min. The hydrogen selenide was evolved slowly and bubbled through the solution in flask B forming sodium selenide. If the temperature of the solution fell below 5° the sodium selenide tended to precipitate as white crystals and clogged the tube leading to burette C. The same thing happened if the concentration of alkali was much above 2 *N*. Some glass wool was placed at the bottom of flask B to catch any solid sodium selenide formed. If the temperature rose much above 10°, the sodium selenide tended to decompose imparting a reddish colour to the solution. A temperature of 5–10° gave the best conditions. The excess of hydrogen selenide, after the preparation of sodium selenide, was removed by passing carbon dioxide through the flask B into the long rubber exit tube.

### *Precipitation of selenides*

A measured volume of the metallic salt sample solution was placed in the beaker D which was cooled to about 10°. After the air in the cabinet had been removed by passing carbon dioxide, a measured volume of the sodium selenide solution was added from burette C (provided with an outlet tube at the top to allow displacement of the carbon dioxide and introduction of sodium selenide). The solution of the seleno salt was stirred for a few seconds with carbon dioxide and a measured volume of hydrochloric acid or acetic acid was then added through a thistle funnel to decompose the seleno salt (if formed) and precipitate the insoluble selenide. The insoluble selenide was quickly and completely precipitated in an easily filterable form without heating. A current of carbon dioxide was then passed into the mixture for stirring and to remove completely the hydrogen selenide evolved. The beaker was then removed from the cabinet, the mixture was filtered through a sintered glass crucible (porosity G 4) and the precipitate was washed successively with water, alcohol and ether, sucked dry for 15 min at the filter pump, dried in a vacuum desiccator for about 30–35 min and weighed.

### *Materials*

The materials used in the various determinations were usually obtained from E. Merck, B.D.H. (AnalaR), or Kahlbaum, and the solutions prepared were carefully standardized by reliable methods.

It was considered desirable to make a thermogravimetric study of the selenides precipitated in order to obtain definite information regarding the correct conditions for weighing. The results so obtained are described below. A standard Stanton Thermobalance was used; details of its working have been given previously[3]. The reagents used and the methods followed in preparing precipitates for thermogravimetric studies were the same as in the gravimetric determination.

## *Determination of elements*

### *Arsenic*

Solutions of sodium arsenate were prepared and standardized by Volhard's method[4] or by the sodium sulphide method[2]. Aliquots of the solutions were then treated with excess of the freshly prepared 2 *N* sodium selenide solution, about 25 ml of the alkali selenide solution being required for every 50 mg of arsenic. The clear solution was then treated with sufficient hydrochloric acid (12 *N*) to neutralize the alkali and to give a final concentration of approximately 6 *N* hydrochloric acid. The mixture was left in the ice-cold water and stirred thoroughly with carbon dioxide. The precipitate of arsenic selenide, brick-red in colour, was then filtered and treated as in the above general method. The weight of the precipitate corresponded to the formula $As_2Se_5$. In some experiments the precipitate of arsenic selenide was also washed with carbon disulphide but there was no change in weight, which shows that no precipitation of free selenium occurred.

Typical results obtained by this procedure are shown in Table I.

The air-dried sample of arsenic pentaselenide gave a horizontal level up to 410°. From this temperature the selenide began to sublime and the sublimation was com-

TABLE I

WITH 2 *N* SODIUM SELENIDE REAGENT

| *Arsenate solution* (*ml*) | *Reagent added* (*ml*) | *12 N HCl added* (*ml*) | *Weight of ppt. $As_2Se_5$* (*g*) | *As found* (*g*) | *As present* (*g*) |
|---|---|---|---|---|---|
| 25 | 35 | 45 | 0.2512 | 0.06908 | 0.06903 |
| 25 | 40 | 55 | 0.2513 | 0.06911 | |
| 25 | 35 | 50 | 0.2512 | 0.06908 | |
| 20 | 18 | 25 | 0.1280 | 0.03521 | 0.03520 |
| 20 | 20 | 30 | 0.1280 | 0.03521 | |
| 20 | 20 | 35 | 0.1281 | 0.03523 | |
| 10 | 15 | 20 | 0.1003 | 0.02758 | 0.02754 |
| 10 | 15 | 20 | 0.1003 | 0.02758 | |
| 10 | 10 | 15 | 0.1002 | 0.02755 | |

pleted at 550°. At this temperature the crucible was found to be empty (Fig. 2).

### *Tin*

A pure sample of metallic tin was dissolved in concentrated hydrochloric acid and oxidized with bromine and the solution of stannic chloride was standardized by the cupferron[5], ammonia[4] or the sodium sulphide method[1]. Aliquots of this solution were treated with ammonium hydroxide until a white precipitate of stannic hydroxide appeared and then with excess of the selenide reagent. This gave a brownish-yellow solution of sodium seleno-stannate, which was then decomposed by excess of 4 $N$ hydrochloric acid to form a reddish brown precipitate. The mixture was cooled in ice-cold water and the precipitate of tin selenide filtered and treated as in the general method. The weight of the precipitate corresponded to the formula $SnSe_2$.

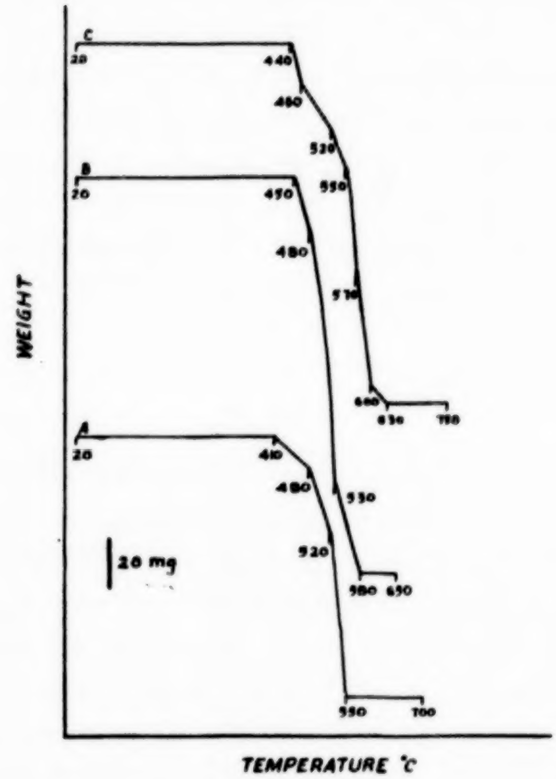

Fig. 2. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, arsenic pentaselenide; B, rhenium heptaselenide; C, mercuric selenide.

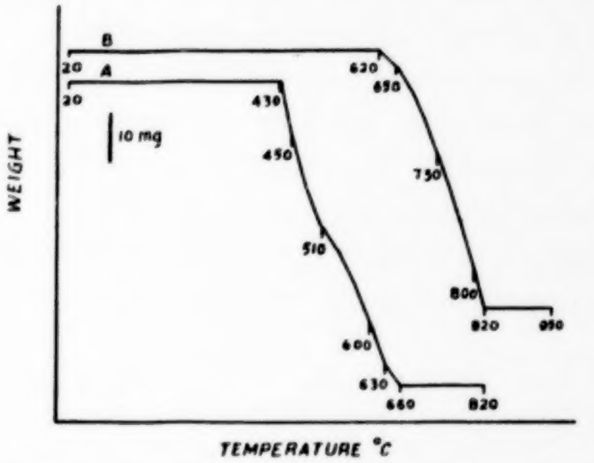

Fig. 3. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, antimony pentaselenide; B, silver selenide.

The solution of sodium seleno-stannate should be decomposed with sufficient 4 $N$ hydrochloric acid to give a final acidity of 1–2 $N$. If more acid is used the precipitate tends to pass through the filter.

### *Antimony*

A solution of potassium hydrogen antimonate was prepared and standardized by reduction with mercury[6] and titration with potassium bromate[7] or by the sodium sulphide method[2]. Aliquots of this solution were treated with the selenide reagent and the seleno salt formed was decomposed with an excess of 4 $N$ hydrochloric acid. The mixture was then cooled and the brown precipitate of antimony selenide was filtered, and treated as in the general procedure. The weight of the precipitate corresponded to the formula $Sb_2Se_5$.

Antimony cannot be determined as selenide from antimony potassium tartrate solution, because sodium selenide forms metallic selenium with sodium tartrate.

An air-dried sample of antimony pentaselenide gave a horizontal up to 430° and then lost weight. The loss was complete at 660° and a horizontal was obtained beyond 660° corresponding to $Sb_2O_4$. The antimony formed by the decomposition of the pentaselenide was oxidized immediately to $Sb_2O_4$. The behaviour of antimony selenide therefore corresponded to that of the sulphide[3] (Fig. 3).

### *Platinum*

Solutions of platinic chloride were standardized by reduction to metal with formic acid[8] or by the sodium sulphide method[2]. Aliquots were neutralized with a cold sodium hydroxide solution and treated with the selenide reagent. The solution containing the seleno salt was acidified with a large excess of acetic acid, stirred well with carbon dioxide, cooled in iced water and treated with about 5 g of ammonium acetate. (If hydrochloric acid was used instead of acetic acid the precipitate tended to pass through the filter). The black precipitate of platinum selenide was filtered at a low pressure and treated as in the general procedure. The ratio of the weight of the metal to that of the precipitated selenide was always found to be 0.4403 which corresponds exactly to the formula $PtSe_2 \cdot 5\ H_2O$.

An oven-dried sample of platinum selenide lost weight from 220° to 500°. From 500° to 700° there was a horizontal corresponding to the weight of the metal (Fig. 4).

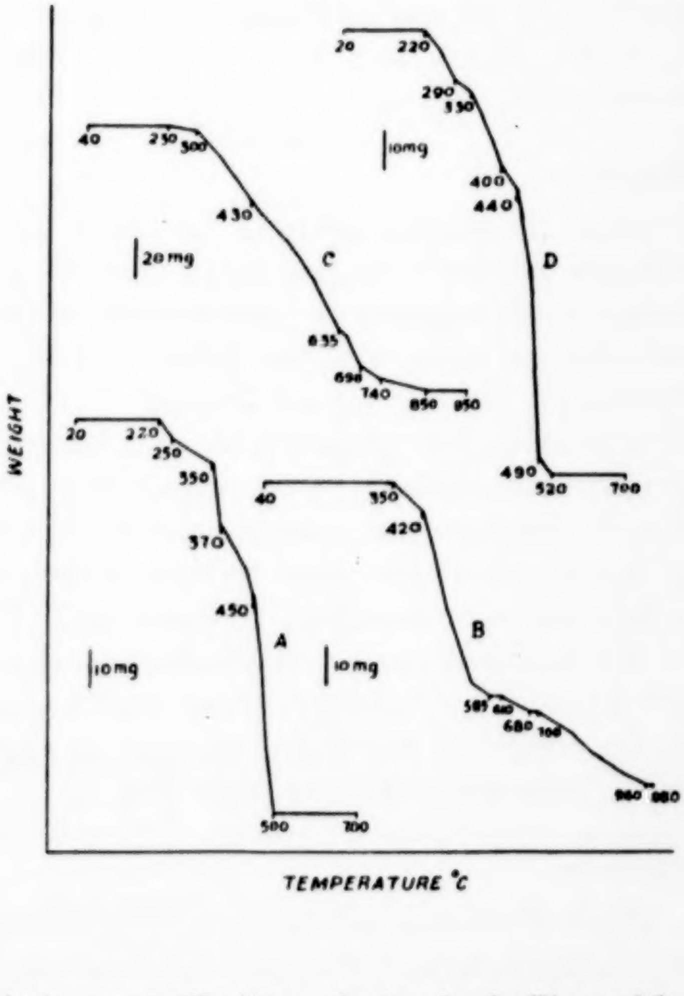

Fig. 4. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, platinum selenide; B, palladium selenide; C, rhodium selenide; D, ruthenium selenide.

### *Ruthenium*

Ruthenium can be precipitated as metal[9] from an alkaline solution by boiling with alcohol. The precipitated metal is ignited and cooled in a current of hydrogen and weighed. If ruthenium selenide is precipitated by treating the solution with sodium selenide and acetic acid successively it can be weighed directly after washing with alcohol and ether, and the whole determination is completed in about 3 h.

Solutions were prepared and standardized by the sodium sulphide method[2]. Aliquots of the solution were made slightly alkaline with a cold solution of sodium hydroxide, then treated with a large excess of the selenide reagent followed by acetic acid in excess and about 10 g of ammonium acetate. The precipitate was then treated as usual. The ratio of the weight of the metal to that of the precipitate was always found to be 0.4267 which corresponds exactly to the formula $Ru_2Se_3 \cdot 2\ H_2O$.

An oven-dried sample of ruthenium selenide lost weight from 220° to 520°. From 520° to 700° there was a horizontal which corresponded to the weight of the metal. Because of spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

### *Palladium*

Solutions of palladium chloride were prepared in dilute hydrochloric acid and standardized by the dimethylglyoxime method[10] or the sodium sulphide method[2]. Aliquots were neutralized with ammonium hydroxide and treated with the selenide reagent. The determination was then completed as for platinum. The weight of the black precipitate of palladium selenide corresponds to the formula PdSe.

The air-dried sample of palladium selenide gave a horizontal up to 350° and then lost weight. There were two horizontals from 585° to 610° and 680° to 700°. These horizontals did not correspond to any exact formula. The loss in weight continued up to 960° after which there was a horizontal up to 980° corresponding to the weight of the metal (Fig. 4).

### *Rhodium*

In all the known methods for the determination of rhodium, except the sodium sulphide method[2], the precipitate must be ignited and cooled in a current of hydrogen before being weighed. A careful study of the behaviour of rhodium salts with sodium selenide and acetic acid has shown that the precipitate of the selenide, after suitable treatment, can be weighed directly.

A solution was prepared by dissolving rhodium chloride in dilute hydrochloric acid and standardized by the formic acid method[11] or by the sodium sulphide method[2]. The determination as selenide was done in the same way as for palladium. The ratio of the weight of the metal to that of the precipitate was always found to be 0.3001 which corresponds exactly to the formula $Rh_2Se_3 \cdot 3\ H_2Se$.

The air-dried sample of rhodium selenide gave a horizontal up to 230° and lost weight from 230° to 850°. From 850° to 950° there was a horizontal corresponding to the weight of the metal. Because of slight spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

### *Rhenium*

Rhenium forms, on treatment with sodium sulphide, a thio salt[2] which decomposes on acidification to precipitate the heptasulphide. Similarly, rhenium forms, on treatment with sodium selenide, a seleno salt which decomposes on acidification to yield heptaselenide. Treatment with acetic acid and ammonium acetate fails to decompose the seleno salt completely and gives low results, but treatment with excess of concentrated hydrochloric acid is satisfactory.

A solution of perrhenate was standardized by the sulphide–nitron method[12] or the sodium sulphide method[2]. Aliquots were treated with the selenide reagent, followed by a large excess of 12 *N* hydrochloric acid. The selenide was completely precipitated without heating (unlike sulphide[2]) and the precipitate settled easily on cooling in ice-cold water. The black precipitate of the selenide was filtered, washed, dried and weighed as in the case of platinum. Its weight corresponded to the formula $Re_2Se_7$.

The air-dried sample of rhenium heptaselenide gave a horizontal up to 450°. There was a steady loss in weight from 450° to 580° and at 580° the crucible was found to be empty (Fig. 2).

### *Mercury*

Solutions of mercuric chloride were standardized by VOLHARD's method[13] or by the sodium sulphide method[2]. Aliquots were treated with ammonium hydroxide until a slight turbidity appeared and then with an excess of the selenide reagent. The formation of the seleno salt of mercury with sodium selenide required a large excess of reagent and vigorous shaking. The mixture was acidified with 6 *N* hydrochloric acid (final acidity 3 *N*) and cooled in ice-water. The black precipitate of mercuric selenide was then filtered and treated as in the general procedure. Its weight corresponded to the formula HgSe.

The air-dried sample of mercuric selenide was stable up to 440°. A rapid loss in weight then ensued up to 630° when the crucible was found to be empty (Fig. 2).

TABLE II

DETERMINATION OF METALS AS SELENIDES

| *Metal* | *Amount of metal* (g) | *Error* % |
|---|---|---|
| Arsenic | 0.0690–0.0176 | +0.03–+0.20 |
| Antimony | 0.0693–0.0181 | +0.03–+0.20 |
| Tin | 0.0783–0.0250 | +0.05–+0.30 |
| Platinum | 0.0420–0.0105 | +0.05–+0.35 |
| Palladium | 0.0628–0.0230 | +0.10–+0.30 |
| Rhodium | 0.0285–0.0072 | +0.07–+0.35 |
| Ruthenium | 0.0592–0.0148 | +0.06–+0.25 |
| Rhenium | 0.0347–0.0131 | +0.10–+0.35 |
| Mercury | 0.1479–0.0300 | +0.06–+0.30 |
| Silver | 0.0874–0.0262 | +0.04–+0.25 |
| Gold | 0.0595–0.0149 | +0.02–+0.10 |

TABLE III

METAL SULPHIDES AND SELENIDES FORMED

| *Salt* | *Arsenic* | *Antimony* | *Tin* | *Rhenium* | *Mercury* | *Silver* | *Platinum* | *Palladium* | *Rhodium* | *Gold* | *Ruthenium* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Thio salt | $As_2S_5$ | $Sb_2S_5$ | $SnS_2 \cdot 2\,H_2O$ | $Re_2S_7$ | $HgS$ | $Ag_2S$ | $PtS_2 \cdot 5\,H_2O$ | $PdS \cdot 2\,H_2O$ | $Rh_2S_3 \cdot 3\,H_2S$ | $Au_2S_3$ | $Ru_2S_3 \cdot 2\,H_2O$ |
| Seleno salt | $As_2Se_5$ | $Sb_2Se_5$ | $SnSe_2$ | $Re_2Se_7$ | $HgSe$ | $Ag_2Se$ | $PtSe_2 \cdot 5\,H_2O$ | $PdSe$ | $Rh_2Se_3 \cdot 3\,H_2Se$ | $Au_2Se_3 \cdot H_2Se$ | $Ru_2Se_3 \cdot 2\,H_2O$ |

### *Silver*

Solutions of silver nitrate were standardized by VOLHARD's method[11] or by weighing as silver chloride[14]. Aliquots were treated with ammonium hydroxide until a clear solution was obtained, and then with an excess of the selenide reagent, stirred well and cooled in ice-cold water. The brownish-black precipitate was filtered and treated as in the general procedure. The weight corresponded to the formula $Ag_2Se$.

The air-dried sample of silver selenide gave a horizontal up to 620°. A rapid loss in weight followed up to 820°. The horizontal from 820° corresponded to the weight of the metal (Fig. 3).

### *Gold*

The well-known method for the gravimetric determination of gold depends on reduction and weighing as the metal. The reduction method takes 6–12 h, depending on the reducing agent used; the method described below requires 3 h and gives results which are as accurate as those obtained by reduction.

Solutions were standardized by precipitating the metal either with sulphur dioxide[15] in an acid medium or with hydrogen peroxide[11] in an alkaline medium. Aliquots were made alkaline with a cold solution of sodium hydroxide, treated with the selenide reagent and shaken thoroughly. An excess of 6 *N* hydrochloric acid was then added and the black selenide was treated as in the general procedure. The ratio of the weight

TABLE IV

| *Weight of $Ag_2Se$ taken (mg)* | *Weight of Ag calculated (820°–950°) (mg)* | *Weight of Ag from graph (820°–950°) (mg)* |
|---|---|---|
| 190 | 140 | 140 |
| 427 | 313 | 312 |
| 118 | 57 | 56 |
| 232 | 112 | 110 |
| *Weight of $PtSe_2 \cdot 5\ H_2O$ taken (mg)* | *Weight of Pt calculated (500°–700°) (mg)* | *Weight of Pt from graph (500°–700°) (mg)* |
| 315 | 139 | 140 |
| 165 | 72 | 73 |
| *Weight of PdSe taken (mg)* | *Weight of Pd calculated (960°–980°) (mg)* | *Weight of Pd from graph (960°–980°) (mg)* |
| 200 | 115 | 116 |
| 213 | 123 | 124 |
| *Weight of $Ru_2Se_3 \cdot 2\ H_2O$ taken (mg)* | *Weight of Ru calculated (520°–700°) (mg)* | *Weight of Ru from graph (520°–700°) (mg)* |
| 194 | 83 | 81 |
| 162 | 69 | 67 |
| *Weight of $Rh_2Se_3 \cdot 3\ H_2Se$ taken (mg)* | *Weight of Rh calculated (850°–950°) (mg)* | *Weight of Rh from graph (850°–950°) (mg)* |
| 216 | 65 | 66 |
| 197 | 59 | 60 |

of the metal to that of the precipitate was found to be 0.5538 which corresponds exactly to the formula $Au_2Se_3 \cdot H_2Se$.

The amounts of metal involved in the determinations and the percentage errors are shown in Table II. The compounds formed by sulphides and selenides in the case of different metals are given in Table III for comparison.

The thermogravimetric studies showed that the precipitates of $As_2Se_5$, $Re_2Se_7$ and HgSe sublime at a particular temperature, while $Sb_2Se_5$ is converted to $Sb_2O_4$ and $Ag_2Se$, $PtSe_2 \cdot 5\ H_2O$, PdSe, $Rh_2Se_3 \cdot 3\ H_2Se$ and $Ru_2Se_3 \cdot 2\ H_2O$ are converted to their metals (as in the case of the corresponding sulphides[3]).

The weights calculated and those actually obtained on heating $Sb_2Se_5$, $Ag_2Se$, $PtSe_2 \cdot 5\ H_2O$, PdSe, $Rh_2Se_3 \cdot 3\ H_2Se$ and $Ru_2Se_3 \cdot 2\ H_2O$ are given in Table IV.

## ACKNOWLEDGEMENT

The authors are grateful to the Council of Scientific and Industrial Research, Government of India, for the grant which enabled this work to be carried out.

## SUMMARY

The gravimetric determination of metals as selenides is proposed. Owing to the rapid atmospheric oxidation of sodium selenide and the toxic nature of hydrogen selenide, special apparatus is required. The methods are analogous to precipitation of sulphides. Arsenic, tin, antimony, platinum, ruthenium, palladium, rhodium, rhenium, mercury, silver and gold can be determined. The thermolysis of precipitates formed with arsenic, antimony, mercury, silver, rhenium, platinum, ruthenium, palladium and rhodium has been studied.

## RÉSUMÉ

Les auteurs ont effectué une étude sur le dosage gravimétrique de métaux sous forme de séléniures. L'arsenic, l'étain, l'antimoine, le platine, le ruthénium, le palladium, le rhodium, le rhénium, le mercure, l'argent et l'or ont pu être ainsi dosés.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die gravimetrische Bestimmung von Arsen, Antimon, Zinn, Platin, Ruthenium, Palladium, Rhodium, Rhenium, Quecksilber, Silber und Gold als Selenide und das thermolytische Verhalten dieser Selenide.

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# ELIMINATION OF DISTILLATION IN THE KJELDAHL METHOD FOR THE MICRO- AND SEMIMICRO-DETERMINATION OF NITROGEN IN NITRO, NITROSO AND AZO COMPOUNDS

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(Received March 4th, 1961)

The determination of nitrogen in nitro, nitroso, and azo compounds by the direct application of Kjeldahl's method leads to low results, particularly when the content of nitrogen attached to oxygen exceeds 10%[1]. Many reagents have, therefore, been suggested for reduction of these types of nitrogen before the Kjeldahl digestion. The reduced nitrogen is then converted to ammonium sulphate from which ammonia is distilled and titrated.

It has been shown, however, that the distillation step in the Kjeldahl method can be eliminated advantageously. This can be achieved by employing either the formaldehyde reaction[2] or the determination of ammonia[3] with hypochlorite. Nitrogen has been determined by the latter method in organic compounds on the sub-micro[4], micro, semimicro[5] and macro scales and in agricultural and animal products[6].

Clearly, the possibility of determining nitrogen in nitro groups, etc., in organic compounds would make this method much more widely applicable. This required an investigation of the various reducing agents with a particular view to determining nitrogen eventually by the hypochlorite method. Some of the reductants successfully used in the usual Kjeldahl method are thiosalicylic acid[7], aromatic hydroxy compounds[8], phenol and zinc dust[9], zinc in methanol and hydrochloric acid[10], zinc alone[11], potassium persulphate and zinc dust[12], stannous chloride[13], sulphur[14], iron and aluminium[15]. Hydriodic acid[16] and various carbohydrates[17,18] have also been employed. Recent work in the field, particularly by BRADSTREET[18], indicates that sucrose brings about a quantitative reduction of oxygen-bound nitrogen in organic nitrogenous compounds.

We have shown that either glucose or zinc in methanol and hydrochloric acid is quite effective as a reductant and provides no interference in the later procedure. Glucose is particularly effective for the quantitative reduction of nitro, nitroso or azo groups in a large number of compounds having different amounts of nitrogen.

## EXPERIMENTAL

### *Reagents*

All the reagents used were of analytical reagent grade.

*Special apparatus: digestion and titration vessels*

A 250-ml round-bottom flask with a $B_{19}$ socket and a 15 cm long $B_{19}$ cone were used for the semi-micro procedure; for micro determinations the volume of the flask was reduced to 100 ml. The flasks attached to their cones served for the reduction and digestion. On completion of the digestion, the cones were detached and the flasks were employed for the titration step.

## MICRODETERMINATION OF NITROGEN

### *Procedure for reduction*

*(1) Reduction with glucose*

Weigh about 4–6 mg of sample into the flask. Add 0.7 g of the catalyst (a mixture of 0.625 g of potassium sulphate with 0.075 g of mercuric sulphate), 0.2–0.3 g of glucose and 3 ml of concentrated sulphuric acid, followed by a few pieces of alundum to aid smooth boiling. Attach the cone to the flask and heat gently on the usual digestion rack for 30 min. Then heat at the boiling temperature of the acid for another 2 h to effect complete decomposition of the substance.

*(2) Reduction with zinc*

Weigh 4–6 mg of sample into the flask. Add 1 ml of glacial acetic acid and warm to dissolve the substance. Add 0.1 g of zinc dust followed by 1 ml of methanol down the wall of the flask to rinse down the zinc dust. Then add hydrochloric acid, a few drops at a time, boiling the solution for 2 min after each addition. Add a total of 2 ml of hydrochloric acid in this way.

Attach the cone and evaporate the bulk of the contents of the flask by boiling, on the digestion rack, in the presence of a few alundum pieces. Do not evaporate to dryness. Add 1.5 ml of concentrated sulphuric acid and continue boiling for 15 min to drive out most of the previously added reagents. Cool the flask and detach the cone. Add 0.7 g of the catalyst (a mixture of 0.625 g of potassium sulphate and 0.075 g of mercuric sulphate) and 1 ml of sulphuric acid. Then reattach the cone and digest for 2 h.

### *Procedure for the determination of nitrogen*

Cool the digest and dilute it about four-fold with water, rinsing the cone with this water. Add 60% sodium hydroxide solution dropwise with occasional shaking of the solution until the appearance of a yellow precipitate of mercuric oxide. Cool the solution and neutralize completely by gradual addition of sodium bicarbonate. Add about 2 g of potassium bromide and shake the flask again until an almost clear solution is obtained.

Run in an excess of 0.02 *N* sodium hypochlorite solution until the solution turns pale yellow. After 5 min add a known excess of 0.01 *N* arsenious oxide solution. Then back-titrate the excess of arsenite with the hypochlorite solution using aqueous 0.05% tartrazine indicator. Carry out a blank determination in the same way.

## SEMIMICRO-DETERMINATION OF NITROGEN

In the case of glucose reduction for the semimicro-determination, 30–50 mg of the sample were taken and 1 g of glucose, 2.8 g of the catalyst (2.5 g of potassium sulphate and 0.3 g mercuric sulphate) and 10 ml of sulphuric acid were used. 0.05 *N* sodium hypochlorite and 0.02 *N* arsenious oxide solutions were employed for the titration.

Zinc – hydrochloric acid reduction on the semimicro scale was carried out according to FISH[10].

### *Calculation*

$$1 \text{ ml } 0.02\ N \text{ NaOCl} \equiv 0.0934 \text{ mg } N_2$$

## DISCUSSION

The results in Table I indicate an accurate determination of nitrogen in nitro, nitroso and azo compounds when the reduction of these groups is effected with glucose. The method employing glucose is easy, neat and less time-consuming. Since the distillation step has been eliminated, the time required is less than that of the usual Kjeldahl method[16].

The method employing zinc reduction is more lengthy and involved than the glucose reduction. It can be seen from Table II that reduction with zinc is as widely applicable as that with glucose.

TABLE I

RECOVERY OF NITROGEN BY GLUCOSE REDUCTION

| *No.* | *Compound* | *Required* | *Found* | | |
|---|---|---|---|---|---|
| 1 | *o*-Nitrobenzoic acid | 8.19 | 8.19 | 8.21 | 8.30 |
| 2 | α-Nitroso-β-naphthol | 8.09 | 8.14 | 7.97 | 8.06 |
| 3 | 2,4-Dinitrophenol | 15.22 | 15.0 | 14.89 | 14.91 |
| 4 | Azobenzene | 15.38 | 15.32 | 15.29 | 15.36 |
| 5 | *p*-Nitrobenzoic acid | 8.38 | 8.33 | 8.42 | 8.40 |
| 6 | 5-Nitrosalicylic acid | 7.65 | 7.71 | 7.57 | 7.70 |
| 7 | *o*-Nitrophenol | 10.07 | 10.18 | 10.13 | 10.11 |
| 8 | *p*-Nitrobenzaldehyde | 9.27 | 9.21 | 9.30 | 9.22 |
| 9 | *p*-Nitroaniline | 20.29 | 20.14 | 20.14 | 20.18 |
| 10 | 3,5-Dinitrobenzoic acid | 13.20 | 13.19 | 13.31 | 13.23 |
| 11 | 1,3-Dinitrobenzene | 16.67 | 16.44 | 16.51 | 16.32 |

TABLE II

RECOVERY OF NITROGEN BY ZINC – HYDROCHLORIC ACID REDUCTION

| *No.* | *Compound* | *Required* | *Found* | | |
|---|---|---|---|---|---|
| 1 | α-Nitroso-β-Naphthol | 8.09 | 8.20 | 8.15 | 8.11 |
| 2 | *o*-Nitrophenol | 10.07 | 10.23 | 10.06 | 10.00 |
| 3 | 1,3-Dinitrobenzene | 16.67 | 16.55 | 16.60 | 16.65 |
| 4 | Azobenzene | 15.38 | 15.45 | 15.51 | 15.32 |
| 5 | 2,4-Dinitrophenol | 15.22 | 15.26 | 15.34 | 15.14 |
| 6 | *p*-Nitroaniline | 20.29 | 20.15 | 20.31 | 20.27 |

### *Hydrazine type of nitrogen*

For hydrazine sulphate, *p*-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine and picrolonic acid, reduction with glucose or zinc is ineffective. The results for these compounds are shown in Table III. It is of interest to note that all these compounds contain more than 20% of nitrogen. Somewhat higher recoveries of nitrogen were obtained for hydrazine sulphate with glucose than with zinc–hydrochloric acid reduction.

TABLE III

RECOVERY OF NITROGEN FROM HYDRAZINE TYPE COMPOUNDS BY GLUCOSE OR ZINC–HYDROCHLORIC ACID REDUCTIONS

| *No.* | *Compound* | *Required* | *Found* | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *Reduction with Zn–HCl* | | | *Reduction with glucose* | | |
| 1 | *p*-Nitrophenylhydrazine | 27.43 | 23.35 | 23.44 | 23.60 | 23.10 | 23.17 | 23.11 |
| 2 | 2,4-Dinitrophenylhydrazine | 28.27 | 26.91 | 26.78 | 26.83 | 26.00 | 26.02 | 26.21 |
| 3 | Picrolonic acid | 21.20 | 16.32 | 16.11 | 16.21 | 14.70 | 14.41 | 14.55 |
| 4 | Hydrazine sulphate | 21.54 | 10.00 | 11.51 | 10.11 | 15.20 | 15.46 | 14.41 |

Attempts were made to improve the results for hydrazine type compounds by modifying the reduction. Aromatic aldehydes condense with hydrazine or its salts to form water-insoluble colourless aldazines[19]. It was considered that condensation of an aldehyde with hydrazines would make subsequent reduction more quantitative. An excess of salicylaldehyde in alcohol was, therefore, used for the formation of aldazines from the hydrazine compounds. The resultant products were digested as such with sulphuric acid. No notable improvement was observed in the recovery of nitrogen. The condensation products were further reduced with glucose but again without success. The recovery of nitrogen did not exceed 85% .

## ACKNOWLEDGEMENTS

We wish to thank Prof. R. BELCHER, University of Birmingham (Great Britain) for his guidance, and Dr. KARIMULLAH, Director, West Regional Laboratories, Pakistan Council of Scientific and Industrial Research, and Dr. M. A. AZIM, Director, Panjab University Institute of Chemistry, for providing facilities to carry out this work.

## SUMMARY

A method is described for the determination of nitrogen in nitro, nitroso and azo compounds by a Kjeldahl method without distillation. The compound is reduced with glucose or zinc in methanol and hydrochloric acid. The ammonium sulphate produced after the usual digestion is determined by hypochlorite–arsenite titration. A single vessel is used for reduction, digestion and titration.

## RÉSUMÉ

Une méthode est décrite pour le dosage de l'azote dans des nitro-, nitroso- et azocomposés au moyen d'une méthode de Kjeldahl sans distillation. La substance est réduite au moyen de glucose ou de zinc en milieu méthanol–acide chlorhydrique; le sulfate d'ammonium formé est titré à l'aide d'hypochlorite et d'arsénite.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung des Stickstoffs in Nitro- Nitroso- und Azoverbindungen nach Kjeldahl ohne Destillation. Die Substanz wird mit Glucose oder Zink in methanolhaltiger Salzsäure reduziert und das gebildete Ammoniumsulfat durch Hypochlorit–Arsenit Titration bestimmt. Die Methode versagt bei Hydrazinen und Pikrolonsäure.

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*Anal. Chim. Acta*, 25 (1961) 448–452

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# CATION-EXCHANGE BEHAVIOR OF CALCIUM ON DOWEX 50W-X8

## SEPARATION FROM MIXTURES

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(Received February 10th, 1961)

Systematic studies of the behavior of the alkaline earth metals, barium and strontium, in ion exchange methods have been carried out in this laboratory[1,2]; we have now extended this work to cover calcium.

SCHUBERT *et al.*[3] separated trace amount of beryllium from calcium on Dowex-50 with sulphosalicylic acid (0.02 *M*–0.1 *M*) at pH 3.5–4.5 by selective elution. DAVIS[4] separated calcium from strontium on Zeokarb-225 at pH 4.25 in presence of EDTA (disodium salt) when all the strontium is retained in the column. MORACHIVISKI AND GORDEEVA[5] separated molybdenum from calcium on anion exchanger PE′-9 (in the nitrate or chloride form) when only calcium passed through. Similarly aluminium is separated from calcium on Dowex 2 anion exchange resin in the citrate form[6].

Further cation exchange studies of calcium have not previously been reported. This paper describes systematic studies on the cation exchange behavior of calcium on Dowex 50W-X8 (hydrogen form) following the same pattern as in case of barium and strontium[1,2]. Calcium has been separated from barium(II), copper(II), zinc, cadmium, mercury, and iron(III).

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*Anal. Chim. Acta*, 25 (1961) 452–456

## APPARATUS AND REAGENTS

The apparatus was the same as before.

Calcium nitrate solution (about 5 mg/ml). About 17.7 g of calcium nitrate (Merck) was dissolved in 600 ml of water. The solution was standardised volumetrically by titration with permanganate after precipitation as oxalate. The cation exchange resin was Dowex 50W-X8 (Dow Chemical, Midland, Mich., U.S.A.), 50–100 mesh (hydrogen form). The resin was treated as before.

## EXPERIMENTAL, RESULTS AND DISCUSSION

### *Ion exchange studies*

An aliquot of solution containing 32.65 mg of calcium was used, the procedure being identical with that followed for strontium. The ion exchange behavior towards nitric acid and hydrochloric acid is shown in Fig. 1. Calcium can be quantitatively recovered by elution with 200 ml of nitric acid (2–4 *M*), hydrochloric acid (2–4 *M*), ammonium chloride (2–4 *M*), sodium nitrate (2–3 *M*) and ammonium acetate (1–4 *M*). When the elution peak was observed in a 50-ml fraction other than the first, the particular fraction was further collected in two 25-ml portions to determine the exact position of the peak (*e.g.* with mineral acids). The eluting agents can be arranged in order of increasing efficiency: citric acid < sodium nitrate = ammonium chloride < hydrochloric acid = ammonium acetate = nitric acid. Acetic acid–ammonium acetate mixtures were not satisfactory (No. 6, Table I). The effluent fractions were determined titrimetrically with permanganate. In the case of strong acid eluants, the fractions were evaporated to dryness, then dissolved in water and used directly for analysis. Calcium was directly precipitated as oxalate when sodium nitrate and ammonium chloride or acetate were used as eluting agents.

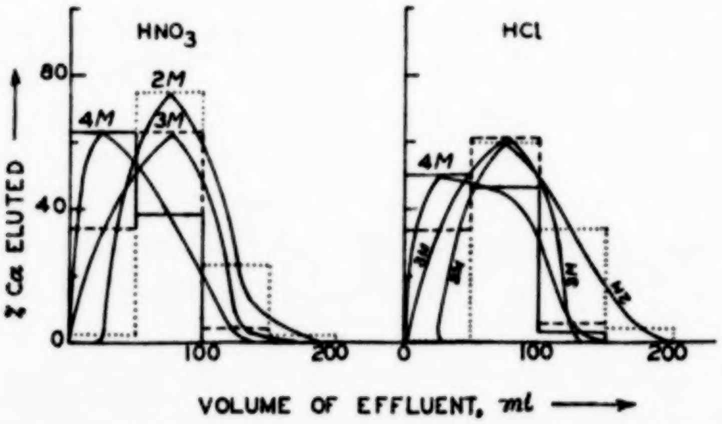

Fig. 1. Cation-exchange behavior of calcium with HCl and $HNO_3$ as eluants.

### *Ion exchange separations*

*Separation from copper, zinc, cadmium, mercury and iron(III).* KEMBER *et al.*[8] studied several organic eluants such as *n*-pentyl alcohol, *n*-propyl alcohol, methyl alcohol, ethyl methyl ketone and acetone. Copper was separated from iron by selective elution with ethyl methyl ketone containing 9% of 1.5 *N* hydrochloric acid. Similarly, copper was separated from nickel with acetone containing 4% hydrochloric acid and 10% water on Zeokarb-225, nickel being retained.

## TABLE I

BEHAVIOR OF CALCIUM TOWARDS VARIOUS ELUTING AGENTS

Calcium = 32.65 mg; weight of oven-dried resin = 12.612 g

| *No.* | *Eluting agent* | *Calcium recovery % (50-ml fraction of effluent)* | | | | *Total calcium recovery %* | *Elution constant E* | *Bed distribution coefficient D = 1/E* |
|---|---|---|---|---|---|---|---|---|
| | | *I* | *II* | *III* | *IV* | | | |
| 1 | $HNO_3$, 1 *M* | — | — | — | 6.66 | 6.66 | — | — |
| | 1.5 *M* | — | 8.78 | 56.92 | 29.06 | 94.76 | 0.2892 | 3.538 |
| | 2 *M* | 1.82 | 75.04 | 22.71 | 1.51 | 101.08 | 0.3812 | 2.623 |
| | 3 *M* | 34.5 | 62.96 | 4.54 | — | 102 | 0.5585 | 1.791 |
| | 4 *M* | 63.11 | 39.34 | — | — | 102.45 | 1.044 | 0.958 |
| 2 | HCl, 1 *M* | — | — | 3.02 | 16.65 | 19.67 | — | — |
| | 1.5 *M* | — | 31.78 | 56.91 | 6.96 | 95.65 | — | — |
| | 2 *M* | 0.9 | 59.02 | 34.5 | 3.93 | 98.35 | 0.3812 | 2.623 |
| | 3 *M* | 33.59 | 60.53 | 5.45 | 1.2 | 100.77 | 0.5585 | 1.791 |
| | 4 *M* | 50.24 | 46.91 | 3.93 | — | 101.08 | 1.044 | 0.958 |
| 3 | $NH_4Cl$, 1 *M* | — | — | 1.5 | 16.81 | 18.31 | — | — |
| | 2 *M* | — | 59.43 | 36.01 | 3.9 | 99.34 | 0.3812 | 2.623 |
| | 3 *M* | 19.51 | 73.21 | 6.3 | — | 99.02 | 0.3812 | 2.623 |
| | 4 *M* | 36.32 | 58.83 | 3.6 | — | 98.75 | 0.3812 | 2.623 |
| 4 | $NaNO_3$, 1 *M* | — | — | 5.7 | 30.01 | 35.71 | — | — |
| | 2 *M* | — | 68.42 | 28.81 | 2.4 | 99.63 | 0.3812 | 2.623 |
| | 3 *M* | 24.01 | 64.52 | 11.4 | — | 99.93 | 0.3812 | 2.623 |
| 5 | $CH_3COONH_4$, 0.5 *M* | — | — | — | — | — | — | — |
| | 1 *M* | — | 27.31 | 57.03 | 14.51 | 98.85 | 0.3812 | 2.623 |
| | 2 *M* | 42.02 | 53.42 | 3.6 | — | 99.04 | 0.3812 | 2.623 |
| | 4 *M* | 53.42 | 39.01 | 9.01 | — | 101.44 | 1.044 | 0.958 |
| 6 | $CH_3COOH + CH_3COONH_4$<br>pH = 4.2 | — | — | 16.81 | 36.6 | 53.41 | — | — |
| 7 | Citric acid (5%)<br>pH = 5.8 | — | — | 18.43 | 44.25 | 62.68 | — | — |

TABLE II

ION-EXCHANGE SEPARATIONS OF CALCIUM

| *No.* | *Foreign ion* | *Added mg* | *Calcium found mg* | *Recovery %* |
|---|---|---|---|---|
| 1 | Cu(II) | 21.6 | 33.12 | 101.4 |
| 2 | Zn(II) | 20 | 33.51 | 102.6 |
| 3 | Cd(II) | 20 | 34.17 | 104.1 |
| 4 | Hg(II) | 20 | 33.6 | 102.9 |
| 5 | Fe(III) | 20.7 | 32.54 | 99.63 |

(Ca = 32.65 mg)

Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II) and iron(III) with 400 ml of 80% acetone which is 1 *N* in hydrochloric acid (Table II). This mixture elutes all these ions but not calcium, which is afterwards eluted with 200 ml of 2 *M* hydrochloric acid. The above mixture partly elutes cobalt(II) (about 60%) and manganese(II) (up to 8%) so that separations from calcium are not quantitative. Similar attempts to separate calcium from nickel and magnesium were not successful, since these metals were not eluted.

*Separation of calcium, strontium and barium.* Calcium can be quantitatively eluted with 200 ml of 1 *M* ammonium acetate which fails to elute barium; this provides an easy method of separation, for barium can later be eluted with 200 ml of 4 *M* ammonium acetate. The effluents were collected in 25-ml fractions, calcium being determined as before, and barium iodometrically. Fig. 2 illustrates the calcium-barium separations obtained. Calcium (9.3 mg) has been separated from as much as 10 times the amount of barium.

The ion-exchange characteristics of strontium and barium on a Dowex 50 column have already been studied. It is interesting to compare the separation factors for barium-calcium and barium-strontium on the basis of their bed distribution coefficients under comparable conditions. The common eluting agents, nitric acid (2-9 *M*), sodium nitrate (2 *M*) and ammonium acetate (4 *M*) were used for these calcula-

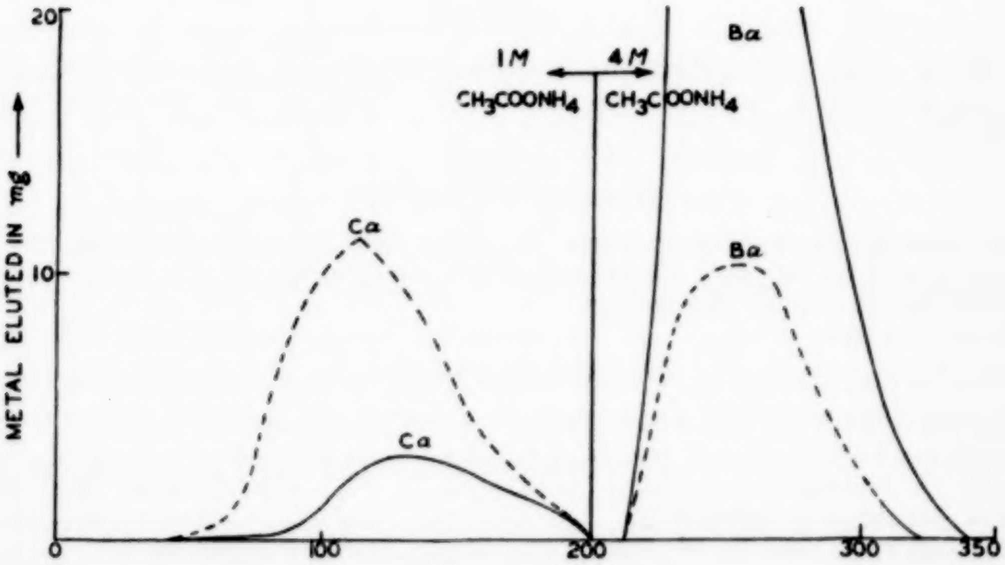

Fig. 2. Separation of barium from calcium.

tions. Table III shows that the best separation of barium from calcium is obtained with 1 $M$ ammonium acetate, since the separation factor is large. Under the same conditions the separation of calcium from strontium is not quantitative; nearly 10% of the strontium accompanies the calcium. This is evident from their $D$-values and has been confirmed experimentally.

TABLE III

SEPARATION FACTORS OF BARIUM–CALCIUM AND BARIUM–STRONTIUM

| *Eluant* | *Bed distribution coefficient* | | | *Separation factor* $D_{Ba}/D_{Ca}$ | *Separation factor* $D_{Ba}/D_{Sr}$ |
|---|---|---|---|---|---|
| | *Barium* | *Strontium* | *Calcium* | | |
| $HNO_3$, 2 $M$ | 2.683 | 3.846 | 2.623 | 1.023 | 0.6996 |
| $HNO_3$, 3 $M$ | 1.872 | 1.136 | 1.791 | 1.045 | 1.647 |
| $HNO_3$, 4 $M$ | 1.06 | 1.136 | 0.958 | 1.107 | 0.933 |
| $NaNO_3$, 2 $M$ | 4.306 | 2.941 | 2.623 | 1.604 | 1.657 |
| $CH_3COONH_4$, 1 $M$ | very large | large | 2.623 | large | small |
| $CH_3COONH_4$, 4 $M$ | 2.683 | 1.136 | 0.958 | 2.801 | 2.361 |

The net operations in this method take 5–6 h. The results are reproducible to ±3%.

## ACKNOWLEDGEMENTS

This work was supported by the Council of Scientific and Industrial Research, India. The authors are grateful to Dow Chemical Co., Midland, Mich., U.S.A., for the gift sample of the resin.

## SUMMARY

The cation-exchange behavior of calcium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid are examined as eluants. Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II), iron(III) and from barium. Separation factors for barium–calcium and barium–strontium are evaluated.

## RÉSUMÉ

Les auteurs ont examiné le comportement du calcium sur échangeur de cations (Dowex 50W-X8), permettant une séparation d'avec Cu, Zn, Cd, Hg(II), Fe(III) et Ba. Des facteurs de séparation Ba–Ca et Ba–Sr sont donnés.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten des Ca bei der Trennung von Cu, Zn, Cd, Hg-(II), Fe-(III) und Ba mit dem Austauscherharz Dowex 50W-X8. Die Trennungskoeffizienten für Ba–Ca und Ba–Sr werden angegeben.

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# A CONTINUOUS FLOW MONITOR FOR SCANNING $^{32}$P-CONTAINING EFFLUENTS FROM CHROMATOGRAPHY COLUMNS*

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(Received March 10th, 1961)

The chromatography of $^{32}$P-labeled materials is highly facilitated by continuous detection of radioactivity in the effluent. Owing to the highly energetic $\beta$-ray emission of $^{32}$P, sensitivity of detection presents no problem and it is therefore possible to do this by a variety of systems. However, certain disadvantages are associated with these systems. Among these are difficulty of decontamination, necessity of special, costly GM tubes and large hold-up volumes.

In our work we have been separating $^{32}$P-labeled phosphate esters by ion exchange chromatography and $^{32}$P-labeled phospholipids by silicic acid chromatography. For this work we have developed an extremely simple and flexible system for monitoring the effluent for radioactivity which is free of the disadvantages mentioned above. It is the purpose of this paper to describe this method.

## CONSTRUCTION

The heart of this system consists of a spiral of plastic capillary tubing positioned just over the mica window of an end-window GM tube. Clay–Adams Intramedic polyethylene tubing serves admirably for this purpose. This tubing is available in a number of sizes ranging between 0.28 and 2.92 mm internal diameter. We have routinely used the size having an internal diameter of slightly over 1 mm. Fig. 1 is a photograph depicting one type of spiral arrangement. The column effluent is led into the tubing by means of either a small standard taper or ball and socket glass joint. The joint is drawn down to a size sufficient to give a tight slide fit into the plastic tubing. Chromatographic columns of the type described by HIRSCH AND AHRENS[1] possess a small ground glass joint which will accept a hypodermic needle. In this case it is possible to insert the proper gauge needle directly into the tubing.

Depending on the availability of shop facilities, a considerable number of arrangements are possible. Our arrangement is that shown in Fig. 1. A cross-sectional diagram of this apparatus is depicted in Fig. 2. The spiral is wound on a set of prongs mounted on a machined brass cylinder. The brass cylinder is equipped with a rod for mounting with a standard laboratory clamp. The bottom of this cylinder is so designed that it makes a slide fit with another machined brass cylinder containing the thin window GM tube mounted in its socket. The two cylinders are held together by spring detents attached to the lower cylinder. These detents seat in a groove as shown in Fig. 2. Intermittent monitoring of the effluent from a number of columns can be accomplished by equipping each with a spiral and shifting a single counting tube from one to another as desired.

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* The work described in this paper was related to the individual programs of the two authors. These investigations were supported by research grants RG5583(C-1) (A.R.K.) and RG-5703(C-1) (L.P.Z.) from the division of General Medical Sciences, Public Health Service.

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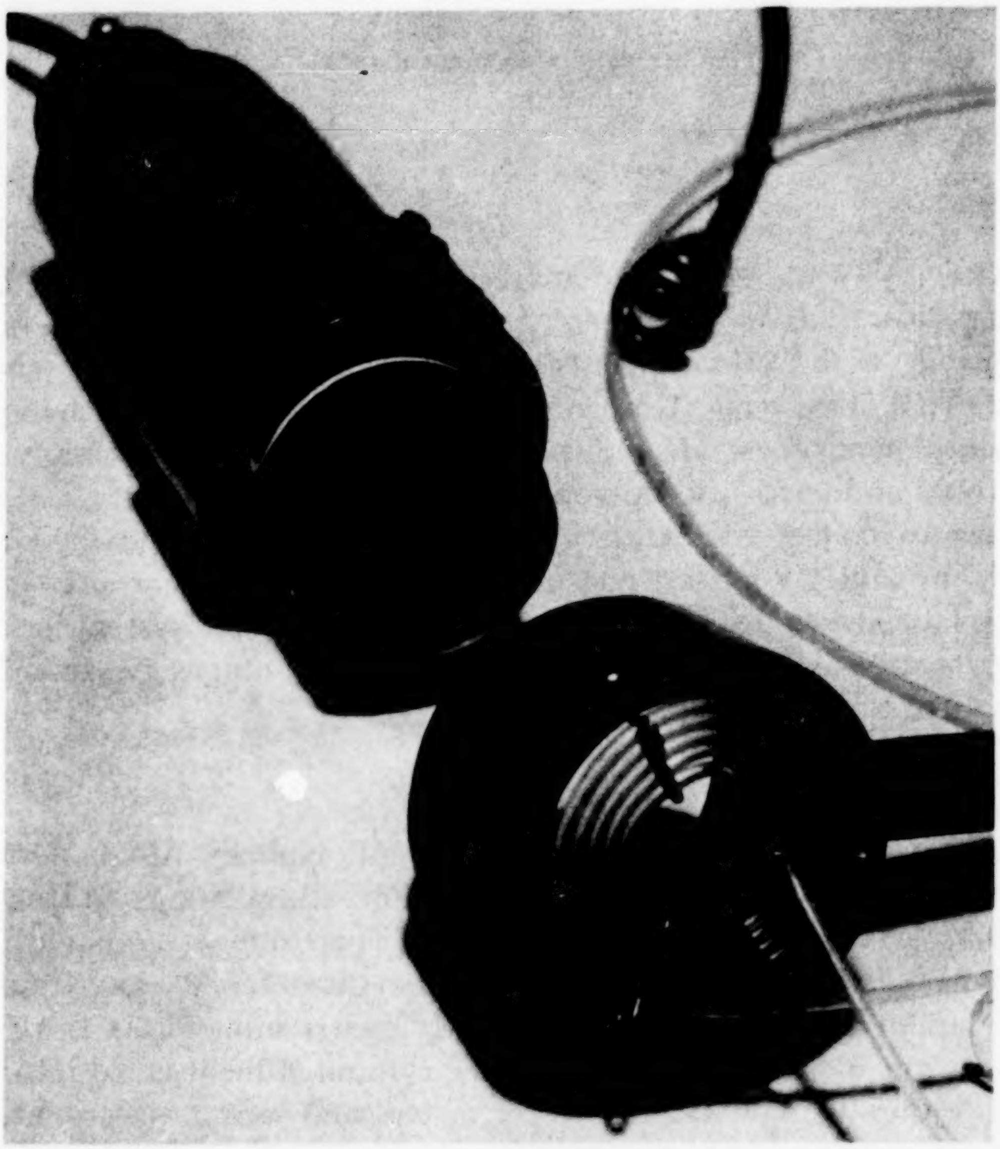

Fig. 1. Photograph of flow monitor, disassembled to show both the GM tube holder and the spiral arrangement.

Since the detector system is ordinarily located in close proximity to the chromatographic column containing the radioactivity, adequate shielding must be provided. The apparatus depicted in Fig. 1 possesses adequate shielding, because of the brass case, except for the end-window itself. Extraneous radiation at this point is excluded by inverting a heavy glass caster cup over the spiral. It is obvious that manifold varieties of lead shielding may also be employed.

In the particular case shown in Fig. 1, the spiral exposed to the counting tube contains 0.8 ml sample volume. The $^{32}P$ in the liquid is counted with approximately 6.2% counting efficiency, essentially the same efficiency with which it would be counted if plated out on a planchet and counted with the same GM tube. Relative sensitivity of detection is apparent from a doubling of the count rate above a 40 counts/min background level when $5 \cdot 10^{-4}$ $\mu$C of $^{32}$P is present in the spiral.

Since absolutely constant flow rates would be essential for the calibration of this system in terms of the actual radioactivity present we have made no attempt to use it for this purpose. Instead, when it was deemed necessary to obtain quantitative data for radioactivity in the column effluents, we have resorted to ancillary methods such as dipping-tube counting or the plating out of representative samples for end-window counting.

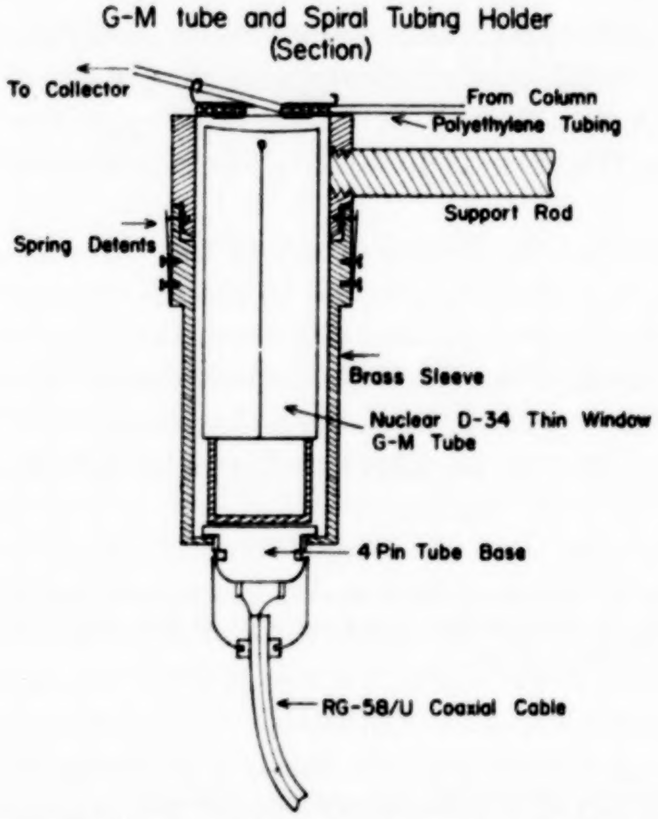
G-M tube and Spiral Tubing Holder
(Section)
To Collector
From Column
Polyethylene Tubing
Support Rod
Spring Detents
Brass Sleeve
Nuclear D-34 Thin Window G-M Tube
4 Pin Tube Base
RG-58/U Coaxial Cable

Fig. 2. Cross sectional diagram of flow monitor showing details of construction.

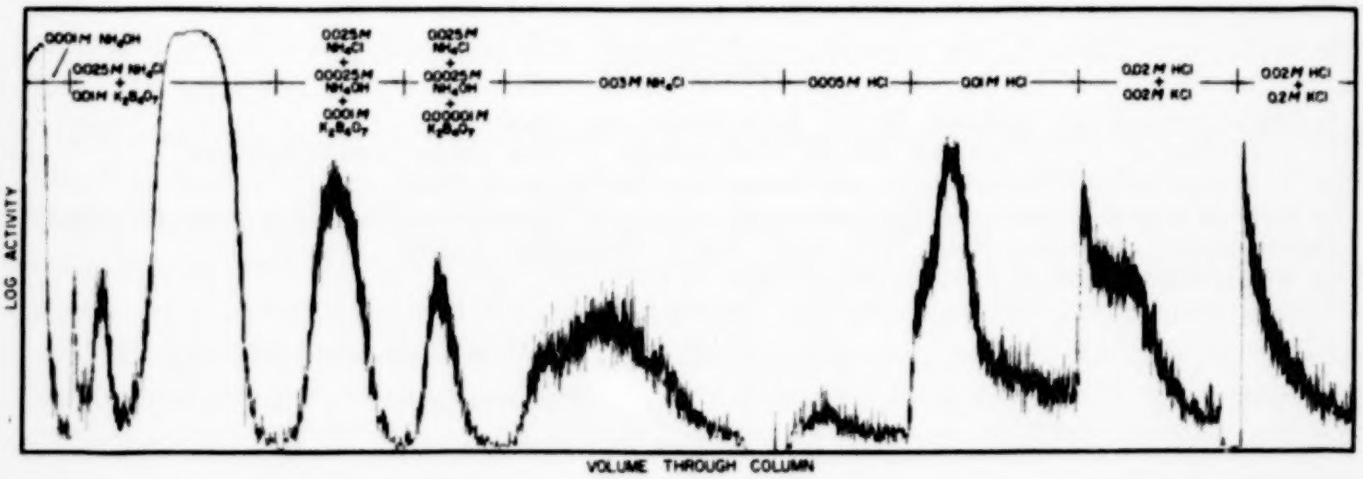

Fig. 3. Separation of $^{32}$P-labeled compounds from Wintex barley by the method of KHYM AND COHN[3].

Chromatographic procedures involving the use of organic solvents, such as the separation of phospholipids[1,2], introduce a possible source of contamination when used with the above described system. This is represented by the leaching out of plasticisers, usually phthalate esters, from the plastic tubing by the organic solvents used as eluents. This situation is circumvented by the use of Teflon tubing. Such tubing, in several sizes, is used as insulation in electronic equipment and is available from electronic supply houses.

Fig. 3 presents a typical application of the system described in this paper. It represents the separation of $^{32}$P-labeled phosphates in a plant extract by the ion exchange system of KHYM AND COHN[3]. Direct monitoring of the effluent permits the collection of several large fractions as dictated by the record of radioactivity appearing on the chart.

Although we have studied the identification of the various materials represented by the peaks in Fig. 3, it is not our purpose to discuss them here. The tracing was obtained by recording the output of a Berkeley count ratemeter on a Weston recorder.

It is unfortunately true that the described system cannot be used for the detection of low-energy $\beta$-rays. Such systems have been described[4,5] but are of considerably greater complexity since they must meet much greater sensitivity demands.

## SUMMARY

A continuous flow monitor for scanning $^{32}$P-containing effluents from chromatography columns is described. The separation of $^{32}$P-labeled compounds from barley is presented as an illustration of the results obtained with the system.

## RÉSUMÉ

Une méthode est proposée permettant, lors de la chromatographie de substances avec phosphore marqué, une détection continue de la radioactivité de l'effluent.

## ZUSAMMENFASSUNG

Beschreibung eines Gerätes, das den Gehalt an $^{32}$P in einem $^{32}$P enthaltenden Effluat einer chromatographischen Kolonne kontinuierlich anzeigt.

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# RINGOFEN-TÜPFELKOLORIMETRISCHER NACHWEIS CARBAMATBILDENDER METALLIONEN NEBEN ALUMINIUM UND ANDEREN METALLEN. I

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(Eingegangen den 24. Februar 1961)

Eine grosse Anzahl analytischer Bestimmungen beruht darauf, dass die aus wässriger Lösung gefällten Metalldithiocarbamate in ein mit Wasser nicht mischbares organisches Lösungsmittel extrahiert und dann bestimmt werden.

Šedivec und Flek[1] haben die Löslichkeit einiger Metalldithiocarbamate in einer Reihe von Solventien bestimmt und festgestellt, dass neben Chloroform besonders Pyridin als Lösungsmittel hervorragend geeignet ist. Da aber Pyridin mit Wasser mischbar ist, ergibt sich die Möglichkeit, einen Metalldithiocarbamatniederschlag in Form eines Tüpfelflecks auf Filterpapier auf dem noch feuchten Papier zum Ring zu waschen, was mit Rücksicht auf die Zersetzlichkeit der Niederschläge sehr erwünscht ist.

Wird nun ein Tüpfelfleck, der neben einem mit Na-DDTC fällbaren eine beliebige Menge eines nicht fällbaren Ions enthält, mit einer Na-DDTC-Lösung besprüht, die nötigenfalls auch Puffersubstanzen und Hilfskomplexbildner enthalten kann, so entsteht sofort ein Niederschlag von Metalldithiocarbamat. Das nicht gefällte Ion kann durch Waschen[2] entfernt und das Metalldithiocarbamat mit Pyridin zum Ring gewaschen werden.

Eine auf diese Weise durchführbare Trennung soll am Beispiel Al–Cu erläutert werden: Ein Tropfen einer Lösung, die neben $Cu^{+2}$ eine beliebige Menge $Al^{+3}$ enthalten darf, wird mit einer Kapillarpipette auf ein Rundfilter Sch & Sch 589[2], 5.5 cm, aufgebracht und mit der Reagenslösung besprüht, die 2% Natriumdiäthyldithiocarbamat, 5% Weinsäure und soviel Ammoniak enthält, dass der pH-Wert zwischen 8 und 9 liegt. Während das $Cu^{+2}$ sofort als Dithiocarbamat gefällt wird, bleibt $Al^{+3}$ als Tartratkomplex in Lösung und wird durch Waschen entfernt. Durch Abpressen mit Filterpapier wird die Hauptmenge der Flüssigkeit entfernt, das Filter auf den Ringofen gelegt und das Kupferdithiocarbamat mit Pyridin in bekannter Weise zum Ring gewaschen[2]. Die grünlich-braune Eigenfarbe des Kupferdithiocarbamatniederschlages kann bereits zum semiquantitativen Nachweis für Kupfer verwendet werden[2]. In Gegenwart anderer, mit Dithiocarbamat fällbarer Ionen, besonders wenn diese gefärbte Niederschläge bilden, muss das Kupfer durch geeignete Trennungsoperationen von störenden Beimengungen befreit werden. Zu diesem Zweck muss die ausserordentlich wirksame Maskierung, die durch die hohe Stabilität der Metalldithiocarbamate bewirkt wird, durch Zerstörung des Dithiocarbamates beseitigt werden.

Am besten geschieht dies durch Räuchern des leicht angefeuchteten Filters über Brom und Ammoniak. Der Überschuss des Oxydationsmittels wird durch kurzes Erwärmen im Trockenschrank oder unter der Trockenlampe unschädlich gemacht. Die Art der weiteren Fällungs- und Auswaschoperation richtet sich nach den zu erwartenden Beimengungen, worüber in Kürze berichtet werden wird. Auf die geschilderte Weise kann nicht nur Kupfer, sondern jedes andere mit Dithiocarbamat fällbare Ion neben beliebigen Mengen eines nicht mitfallenden Ions, wie z.B. Aluminium, nachgewiesen werden. Die Erfassungsgrenze der Bestimmung ist lediglich durch die Mindestmenge gegeben, die mit der gewählten Nachweisreaktion im Ring erfasst werden kann. Selbstverständlich kann durch mehrmaliges wechselweises Auftüpfeln von Probe und Reagens eine Anreicherung des gesuchten Ions erreicht werden.

## ZUSAMMENFASSUNG

Kleine Mengen gewisser Kationen werden durch Na-DDTC in Gegenwart beliebiger Mengen nicht mitfallender Kationen im Tüpfelfleck gefällt und die anderen durch Waschen entfernt. Me-DDTC wird *ohne* vorherige Trocknung mit Pyridin zum Ring gewaschen und das Kation dort — gegebenenfalls nach Entfernung störender Begleiter — nachgewiesen. Die Methode wird am Beispiel Al–Cu erläutert.

## SUMMARY

Small amounts of cations yielding insoluble dithiocarbamates are fixed on filter paper by precipitation with Na-DDTC. Other cations are removed by washing. On the Weisz-Ring oven, the metal-DDTC is moved to the ring by washing with pyridine *without* prior drying. Identification is carried out in the ring zone, if necessary after destruction of carbamate and removal of interfering cations. Cu–Al is given as example.

## RÉSUMÉ

Une méthode à la touche, sur papier filtre, est proposée pour l'identification et le dosage semi-quantitatif de certains cations. La séparation cuivre–aluminium est donnée comme exemple.

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# SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM WITH SOLOCHROMATE FAST RED

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(Received February 3rd, 1961)

## INTRODUCTION

Only a few methods have up till now been reported for the application of azo dyes to the spectrophotometric determination of uranium. CHENG[1], and GILL *et al.*[2] have described a very sensitive method for the determination of trace amounts of uranium employing the azo dye, 1-(2-pyridylazo)-2-naphthol (PAN), while POLLARD *et al.*[3] proposed 4-(2-pyridylazo)-resorcinol as a possible analytical reagent for the colorimetric estimation of cobalt, lead and uranium.

FOREMAN *et al.*[4] showed that the arseno azo dye thorin (sodium salt of 1-(*o*-arsenophenylazo)-2-naphthol-3,6-disulphonic acid, thoron, thoronol) can be applied for the spectrophotometric determination of microgram amounts of uranium(IV). Recently a similar dye, neothorin (3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid; arsenazo) has been introduced as a photometric reagent for the determination of uranium(VI) by FRITZ AND JOHNSON-RICHARD[5] and others[6-8].

Research work in this laboratory showed that among the azo dyes examined, Solochromate Fast Red 3G 200 (C.I. Mordant Red 19; 6-amino-4-chloro-1-phenol-2-sulfonic acid → 3-methyl-1-phenyl-5-pyrazolone) can be employed as a sensitive and relatively specific reagent for the determination of uranium(VI). Owing to the low solubility of this dyestuff in water a number of organic solvents were investigated for their suitability as a medium for the spectrophotometric determination of uranium. The best results were obtained in methanolic medium in which also the solubility of inorganic salts is sufficiently high. By the addition of EDTA it was possible to eliminate interference by small amounts of copper, iron and thorium. Interfering ions which cannot be masked by means of EDTA must be separated from uranium before the final determination with Solochromate Fast Red can be carried out. For the purpose of uranium separation, ion exchange methods have been developed in this laboratory which ensure quantitative removal of the interfering ions[9-14]. Among these methods the separation of uranium from practically all elements by means of column operations in hydrochloric acid–ethanol[13] or –methanol[14] solutions employing the strongly basic anion exchanger Dowex 1 proved to be most suitable.

## SOLUTIONS AND REAGENTS

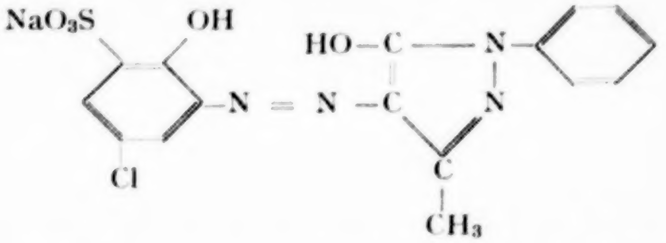
### *Uranium standard solutions*

An exactly weighed amount of reagent grade uranyl nitrate was quantitatively converted to uranyl chloride by repeated evaporation with 6 *N* hydrochloric acid.

The uranyl chloride obtained was dissolved in 1 $N$ hydrochloric acid. This uranium stock solution contained a gravimetrically[15] and volumetrically[16] determined amount of 1 mg uranium/ml of 1 $N$ hydrochloric acid. By dilution with 1 $N$ hydrochloric acid, standard solutions of lower uranium concentrations were prepared.

*Dyestuff solutions*

500 mg of Solochromate Fast Red 3G 200 (this dyestuff was kindly furnished by the Imperial Chemical Industries, Hexagon House, Blackley, Manchester, England) of the following formula:



were dissolved in 100 ml of pure methanol. Since this dyestuff was accompanied by a small amount of inorganic substances insoluble in methanol, it was filtered after digestion for 6 h. This solution will further be referred to as 0.5%. By dilution with methanol 0.25% and 0.1% solutions of the dyestuff were prepared.

*Standard solutions of other ions*

Many solutions of common foreign cations and a number of anions in 1 $N$ hydrochloric acid were applied.

*Organic solvents*

The following solvents, all chemically pure, were employed: methanol, ethanol, $n$-propanol, isopropanol, acetone, ethylene glycol and dioxane.

## APPARATUS

The absorbance measurements were carried out in 1-cm cells using a Beckman spectrophotometer model B. For the preparation of the measuring solutions 10-ml flasks or 25-ml beakers were employed.

## CHOICE OF SUITABLE WAVELENGTH

To 1 ml of a uranium standard solution containing 100 $\mu$g of uranium, 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 $M$ sodium acetate solution were added. This solution was diluted to the mark with methanol and measured against a reagent blank in the wavelength range from 450 to 550 m$\mu$. The results of these measurements are recorded in Fig. 1 from which it is seen that the maximum absorbance of the uranium dyestuff complex is found at 490 m$\mu$.

## INFLUENCE OF ACIDITY

Since no complex formation occurs in hydrochloric acid media, increasing amounts of 2.5 $M$ sodium acetate solution were employed. The solutions contained 100 $\mu$g of uranium dissolved in 1 ml of 1 $N$ hydrochloric acid, 1 ml of the 0.5% dyestuff solution and 0–3.0 ml of the sodium acetate solution. These solutions were diluted to the mark with methanol and measured against reagent blank solutions at 490 m$\mu$. These measurements showed (see Fig. 2) that after a steep increase of absorbance when 0.4–1.0 ml of the sodium acetate solution was present, further addition of sodium acetate had no effect on the absorbance up to an amount of 2.5 ml, whereafter a slight decrease could be noticed. For this reason 1 ml of the sodium acetate solution per 10 ml was applied in all further experiments.

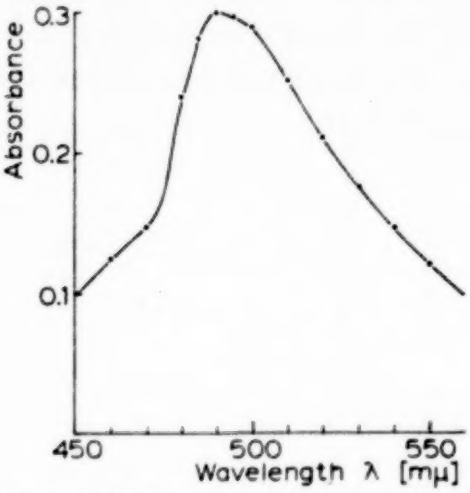


Fig. 1. Choice of suitable wavelength.

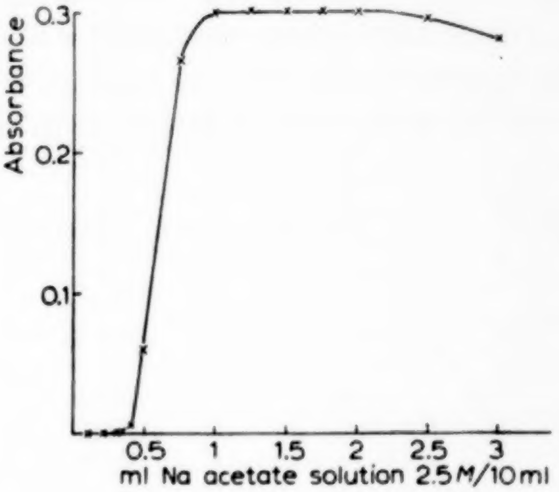


Fig. 2. Influence of acidity.

## INFLUENCE OF DYESTUFF CONCENTRATION

The solutions contained 100 μg of uranium dissolved in 1 ml of 1 *N* hydrochloric acid, 0.5–8.0 ml of the 0.1% dyestuff solution and 1 ml of 2.5 *M* sodium acetate solution. These solutions were diluted to the mark with methanol and measured against reagent blank solutions at 490 mμ. Variations in the dyestuff concentration from 2.5–7.5 ml/10 ml of measuring solution did not change the maximum absorption whereas at lower concentrations the absorbance increased to a maximum in presence of 2.5 ml of the dyestuff solution (see Fig. 3). Consequently 1 ml of a 0.5% dyestuff solution corresponding to 5 ml of the 0.1% solution was used for further work.

## INFLUENCE OF SOLVENTS

Solutions containing 100 μg of uranium in 1 ml of 1 *N* hydrochloric acid, 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 *M* sodium acetate were diluted to the mark with the following solvents: methanol, ethanol, *n*-propanol, isopropanol, ethylene glycol, acetone and dioxane, and measured against corresponding reagent blank solutions at 490 mμ. The results (see Table I) showed that the highest absorbance was reached in methanol and acetone; but in the latter solvent no reproducible results could be obtained.

TABLE I

INFLUENCE OF SOLVENTS

| *Solvent* | *Absorbance at 490 mμ* |
|---|---|
| methanol | 0.300 |
| ethanol | 0.265 |
| *n*-propanol | 0.240 |
| isopropanol | 0.280 |
| ethylene glycol | 0.260 |
| acetone | 0.340 |
| dioxane | 0.290 |

When the organic solvent was replaced by varying amounts of water, it was found that with up to 4 ml of water per 10 ml of measuring solution no change of absorbance could be observed. At higher water concentrations the dyestuff was precipitated.

### INFLUENCE OF TIME, TEMPERATURE AND SEQUENCE OF ADDITION

Experiments showed that the uranium dyestuff complex is of very high stability, the absorbance being constant for at least 24 h. In the range from 10–30° no effect of temperature on the absorbance was noticeable. The sequence of reagent addition should be performed as described in the working procedure.

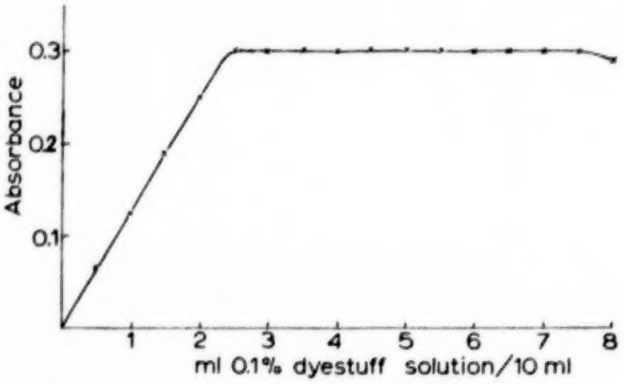


Fig. 3. Influence of dyestuff concentration.

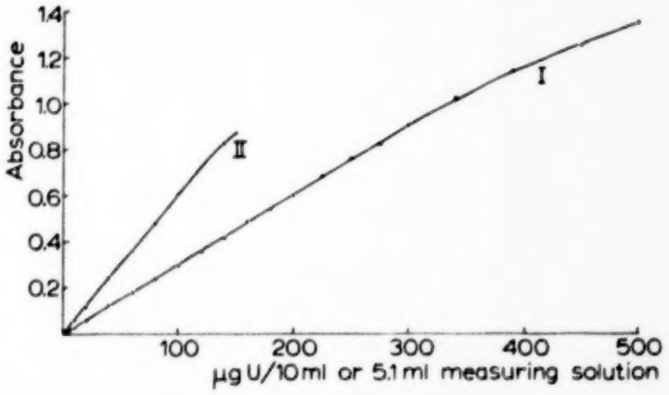


Fig. 4. Calibration curves.

### INFLUENCE OF FOREIGN IONS

In Table II the percentage error of uranium measurements in presence of numerous ions is recorded. All the solutions contained 100 µg of uranium and different amounts of the ions under investigation. They were prepared as described under (*a*) (see working procedure): 1 ml of a uranium standard solution containing 100 µg of uranium and a certain volume of a standard solution of the ion in question were evaporated to dryness on the water bath, etc.

It can be seen that some elements interfere more or less seriously with the uranium determination. In order to remove these ions from uranium the anion exchange separation methods[9-14] mentioned before must be applied, thus making possible uranium determinations in a variety of materials, *e.g.* in marine sediments. Small amounts (up to 100 µg) of iron(III), copper(II) and thorium(IV) are masked by the EDTA present.

### CALIBRATION CURVES

#### *In 10 ml of measuring solution*

The solutions contained 0–500 µg of uranium dissolved in 1 ml of 1 *N* hydrochloric acid, 0.1 ml of 0.1 *M* EDTA, 1 ml of 0.5% dyestuff solution and 1 ml of 2.5 *M* sodium acetate. These solutions were made up to volume with methanol and measured against a reagent blank solution at 490 m$\mu$. From Fig. 4, curve I, it is seen that Beer's law holds from 0–300 µg of uranium.

#### *In 5.1 ml of measuring solution*

The solutions contained 0–150 µg of uranium dissolved in 0.5 ml of 1 *N* hydrochloric acid, 0.1 ml of 0.1 *M* EDTA, 1 ml of 0.25% dyestuff solution, 0.5 ml of 2.5 *M* sodium acetate and 3 ml of methanol. These solutions were then measured against a reagent

## TABLE II

INFLUENCE OF FOREIGN IONS ON URANIUM DETERMINATION

| *Ion* | *Present as* | *Foreign ion (µg)* | *% error* |
|---|---|---|---|
| Mg(II) | chloride | 1000 | + 62.0 |
| Ca(II) | chloride | 1000 | + 56.0 |
| Sr(II) | chloride | 1000 | — 1.0 |
| Ba(II) | chloride | 1000 | + 2.0 |
| Al(III) | chloride | 1000 | +220.0 |
| Sn(II) | chloride | 1000 | — 2.0 |
| Pb(II) | chloride | 1000 | — 3.0 |
| Bi(III) | chloride | 1000 | + 19.0 |
| Cu(II) | chloride | 200 | + 16.0 |
| Cu(II) | chloride | 100 | — 1.0 |
| Zn(II) | chloride | 1000 | — 2.5 |
| Cd(II) | chloride | 1000 | — 1.5 |
| Hg(II) | chloride | 1000 | — 2.0 |
| Y(III) | nitrate | 1000 | +108.5 |
| La(III) | nitrate | 1000 | + 12.0 |
| Ce(III) | sulphate | 1000 | precipitation |
| Nd(III) | nitrate | 1000 | +106.0 |
| Pr(III) | nitrate | 1000 | +112.4 |
| Ti(IV) | chloride | 1000 | +200.0 |
| Zr(IV) | chloride | 1000 | + 80.0 |
| Hf(IV) | chloride | 1000 | + 11.7 |
| Th(IV) | chloride | 1000 | +190.5 |
| Th(IV) | chloride | 100 | + 3.0 |
| V(V) | vanadate | 1000 | +111.0 |
| Cr(III) | sulphate | 1000 | + 19.2 |
| Mo(VI) | molybdate | 1000 | — 2.0 |
| W(VI) | tungstate | 100 | + 2.4 |
| Mn(II) | chloride | 1000 | + 1.0 |
| Fe(III) | chloride | 100 | + 1.0 |
| Fe(III) | chloride | 200 | + 15.0 |
| Co(II) | chloride | 1000 | + 0.8 |
| Ni(II) | chloride | 1000 | + 1.5 |
| Pd(II) | chloride | 1000 | +280.0 |
| Pt(IV) | chloride | 1000 | — 1.5 |
| $Br^-$ | K-salt | 2000 | + 25.0 |
| $I^-$ | K-salt | 2000 | + 2.5 |
| $F^-$ | K-salt | 2000 | + 11.0 |
| $NO_3^-$ | K-salt | 2000 | + 3.0 |
| $SO_4^{-2}$ | K-salt | 2000 | — 25.0 |
| $H_2PO_4^-$ | K-salt | 2000 | — 2.5 |
| $CN^-$ | Na-salt | 2000 | — 2.8 |
| $AsO_4^{-3}$ | Na-salt | 2000 | — 2.0 |
| oxalate | Na-salt | 2000 | — 2.0 |
| tartrate | K-salt | 2000 | + 0.5 |
| citrate[a] | K-salt | 2000 | — 1.0 |
| $SCN^-$ | ammonium salt | 2000 | — 0.5 |

[a] As the addition of citrate does not affect the uranium determination we tried to mask some seriously interfering ions by adding 0.1 ml of a 10% potassium citrate solution per 10 ml measuring solution. The following elements up to 1000 µg can effectively be masked: Th, La, Ce, Y, Nd and Pr. This fact however was not utilized for the development of the working procedure since all the ions recorded in Table II can easily be separated from uranium by means of anion exchange[9–14].

blank solution at 490 mμ. The results are recorded in Fig. 4, curve II, showing that Beer's law applies from 0–120 μg uranium.

## WORKING PROCEDURE

The uranium-containing solution *e.g.* an eluate after an ion exchange separation[9-14], is evaporated in a quartz dish to complete dryness and ignited to remove organic matter. The uranium oxide obtained is then taken up in 5–10 ml of 6 *N* hydrochloric acid and the solution evaporated to dryness on a water bath. The uranyl chloride is transferred quantitatively to a 25-ml beaker using a few ml of 1 *N* hydrochloric acid. This solution is then evaporated to complete dryness on the water bath. The residue is taken up as follows:

(*a*) in 1 ml of 1 *N* hydrochloric acid and left standing for 15 min with intermittent shaking of the beaker. Afterwards 0.1 ml of 0.01 *M* EDTA is added and the solution transferred to a 10-ml measuring flask, rinsing the beaker with altogether 6 ml of methanol. To this solution 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 *M* sodium acetate is added. After making up to volume with methanol, the solution is measured against a reagent blank solution at 490 mμ. By means of the calibration curve in Fig. 4, curve I, the amount of uranium in the measuring solution can be readily determined.

(*b*) in 1 ml of a mixture of 25 ml of 1 *N* hydrochloric acid and 25 ml of methanol and left standing for about 15 min with occasional shaking. Now 0.1 ml of the EDTA solution, 1 ml of 0.25% dyestuff solution, 0.5 ml of sodium acetate solution and 2.5 ml methanol are added. The mixture is homogenised by gently shaking the beaker and is then measured against a reagent blank solution at 490 mμ (the reagent blank solution must be prepared simultaneously). By means of the calibration curve II in Fig. 4 the amount of uranium contained in the measuring solution can readily be determined.

## SENSITIVITY AND ACCURACY

According to curves I and II in Fig. 4, amounts of 5 μg uranium/10 ml or 2.5 μg uranium/5.1 ml of measuring solution can still be determined. The percentage error in the concentration range from 10 to 300 μg of uranium/10 ml has an average value of ±3%. Below 10 μg of uranium the error may increase to ±5–10%. In 5.1 ml measuring solution the average percentage error is ±4% except at concentrations below 5 μg uranium where it reaches a value of ±8–12 %.

TABLE III

DETERMINATION OF URANIUM IN MARINE MATERIALS

| *Sample No.* | *p.p.m. uranium found by polarographic method* | *p.p.m. uranium found by Solochromate Fast Red method* |
|---|---|---|
| 1 | 133 | 136 |
| 2 | 130 | 132 |
| 3 | 130 | 135 |
| 4 | 265 | 270 |
| 5 | 166 | 170 |
| 6 | 115 | 110 |
| 7 | 192 | 200 |
| 8 | 205 | 200 |
| 9 | 151 | 155 |

## APPLICATION

In order to find out whether this method can also be applied to the uranium analysis of marine materials *e.g.* manganese nodules, a number of samples were analysed. After separation and isolation of uranium by means of anion exchange[13,14], the uranium content of the eluates was determined both polarographically[13] and spectrophotometrically with Solochromate Fast Red. The results in Table III show that this spectrophotometric determination is as reliable as the extensively used polarographic method. The latter method is however superior when amounts of less than 1 μg uranium/ml of measuring solution are present.

## ACKNOWLEDGEMENTS

The research reported above was sponsored by the International Atomic Energy Agency and the United States Atomic Energy Commission under contract number 67/US. The generous support from these agencies is gratefully acknowledged. The authors also want to express their sincere appreciation to Prof. G. Arrhenius, University of California, Scripps Institution of Oceanography, La Jolla, California, for furnishing the samples analyzed.

## SUMMARY

A method is described for the spectrophotometric determination of micro amounts of uranyl ions with the azo dye, Solochromate Fast Red, which reacts with uranium(VI) in acetate-buffered methanol solution to form an orange-brown colored complex with maximum extinction at 490 mμ. Beer's law is obeyed over a wide range of uranium concentrations. Only a limited number of foreign ions interfere, hence this method is generally applicable after removal of interfering ions by anion exchange; *e.g.* uranium can be determined in marine materials.

## RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique de microquantités d'uranium(VI), au moyen de rouge au chrome solide. En solution tampon, dans l'alcool méthylique il se forme un complexe brun orange, avec extinction maximum à 490 mμ. Les ions génants sont éliminés au préalable par échangeur d'ions.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Mikromengen Uran mit Solochrom Fast Red, das mit Uran einen orangebraun gefärbten Komplex bildet. Störende Fremdionen können mit einem Ionenaustauscherharz entfernt werden.

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# SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM WITH STANNOUS IODIDE REAGENT

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(Received March 6th, 1961)

KEMBER AND WELLS[1] were able to detect 0.1 p.p.m. of iridium at 360 mμ by the stannous chloride method, but the intensity of color was found to vary considerably with time and temperature (little color developed at room temperature). No method of obtaining reproducible results adequate for colorimetric analysis was found. A serious difficulty was the very high absorbancy of the blank at 360 mμ. BERMAN AND MCBRYDE[2] noted that hexachloroiridate solutions after boiling with hydrobromic acid produced a yellow solution upon the addition of stannous chloride in hydrochloric acid. The absorbancy maximum was at 485 mμ. If the stannous chloride were dissolved in hydrobromic acid, the maximum absorbancy shifted to 402 mμ and the solution was more stable and had a higher absorbancy. The data given indicate that the molar absorptivity is constant in the middle of the absorbancy *versus* concentration curve but decreases at both ends. When stannous bromide was used in place of stannous chloride, the sensitivity was increased by 10%, but the color was less stable.

The above results suggest that as the size of the halogen anion increases, the stannous halide reaction increases in sensitivity and stability. This coincides with the polarizability sequence of the halides of interest: $I^- > Br^- > Cl^-$. BERG AND YOUMANS[3] established this sensitivity order for the stannous halide reaction with rhodium(III). The stannous iodide reaction thus promised a more sensitive and stable analysis of iridium; the present work was undertaken to test that hypothesis.

## EXPERIMENTAL

### *Apparatus and reagents*

The spectra were recorded with a Beckman DK-1 spectrophotometer. Absorbancies at 446 mμ were measured with a Beckman DU spectrophotometer using 1-cm quartz cells.

Iridium(III) solutions were prepared by dissolving the trichloride in 0.3 *N* hydrochloric acid and standardizing by the method of GILCHRIST[4].

Tin(II) chloride solutions were prepared by dissolving 1 part by weight of $SnCl_2 \cdot 2H_2O$ in 1 part by volume of concentrated hydrochloric acid and diluting with 2 parts by volume of distilled water. For acidity calculations, this solution was considered to be 4 *N* in hydrochloric acid. Tin metal was placed in the stock solution.

All other reagents were of analytical grade and prepared as indicated.

### *Recommended procedure*

Transfer the iridium solution to a 25-ml volumetric flask. Add sufficient hydrochloric acid so that the final solution will be 1.3 *N* in HCl. Add 5 ml of 40% (w/v) potassium iodide solution, mix, and heat for 10 min in a boiling water bath. Cool to room temperature. Pipet 2 ml of the stannous chloride solution into the flask and dilute to volume with distilled water. Mix and heat the unstoppered flasks for 3 min in a boiling water bath. Cool immediately to room temperature in an ice bath. Measure the absorbancy of the solution at 446 mμ *versus* a blank prepared identically to the sample except for the omission of iridium. Determine the iridium concentration from a standard curve.

### *Effect of temperature on solution absorbancy*

The iridium is converted to the iodide complex by 10 min of heating with potassium iodide in the boiling water bath (Fig. 1). Upon the addition of tin(II) chloride solution

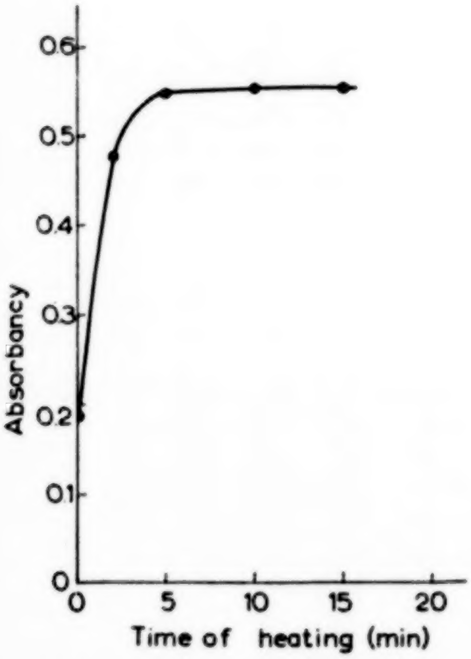

Fig. 1. Effect of time of heating on the conversion of hexachlororiridite to hexaiodoiridite. 7.7 p.p.m. Ir used in the test solution. Absorbancy measured at 446 mμ.

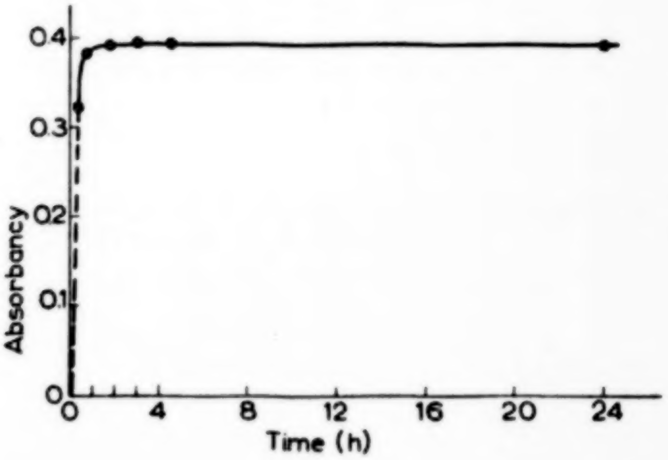

Fig. 2. Variation of solution absorbancy (446 mμ) with time of color development at room temperature. 5.8 p.p.m. Ir used in the test solutions.

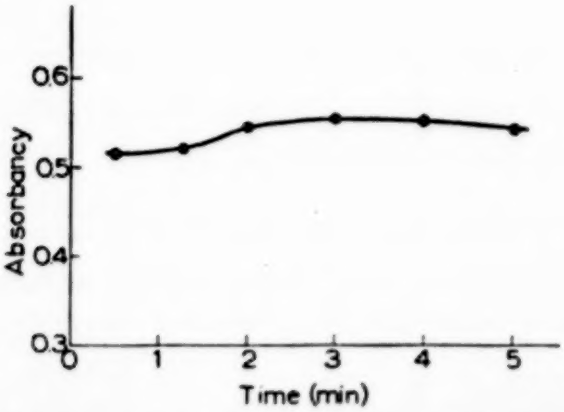

Fig. 3. Variation of solution absorbancy (446 mμ) with time of heating in boiling water bath after the addition of stannous chloride solution and dilution to volume. 7.7 p.p.m. Ir used in the test solutions.

to the hexaiodoiridite, a yellow to brown color developes that attains a maximum absorbancy after 2 h at room temperature (Fig. 2). The complex agrees in molar absorptivity and stability with the complex developed in the boiling water bath. The absorbancy of a solution heated in the water bath varies but little with heating periods of 1–5 min (Fig. 3). The maximum and most reproducible absorbancy is obtained with 3 min heating. Heating was chosen to speed the analyses. The absorbancy peak is at 446 mμ (Fig. 4) and the solution is stable for at least 24 h if kept in the dark.

*Effect of hydrochloric acid concentration on solution absorbancy*

The molar absorptivity of the iridium complex changes little as the hydrochloric acid concentration is changed from 1 to 2 *N* (Fig. 5). A precipitate of $SnI_2$ forms if the acid concentration is below 1 *N*; above 2 *N*, the molar absorptivity of the solution decreases slowly. A solution 1.3 *N* in hydrochloric acid was used in subsequent tests.

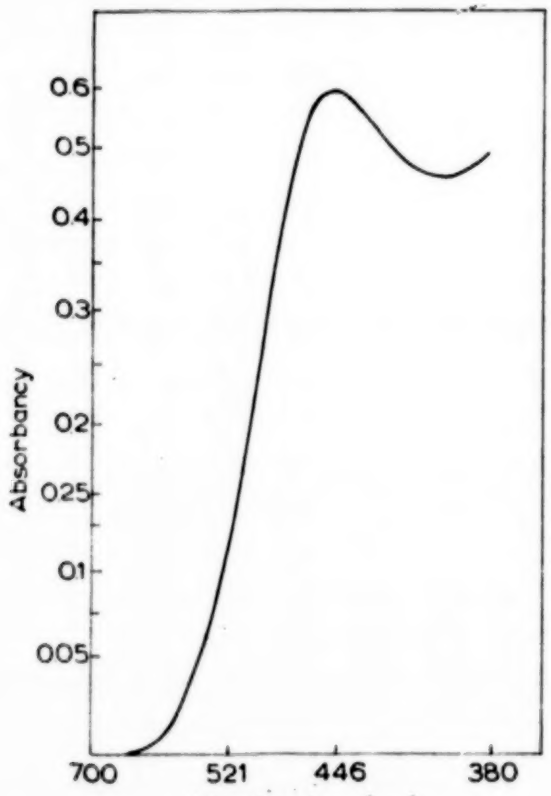

Fig. 4. Absorbancy curve of a stannous iodide iridium iodide solution containing 7 p.p.m. Ir.

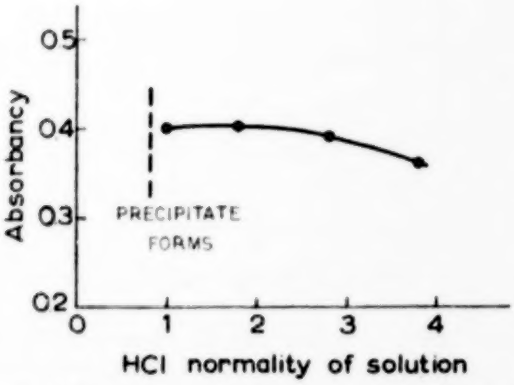

Fig. 5. Variation of solution absorbancy (446 mμ) with concentration of hydrochloric acid. 5.5 p.p.m. Ir used in test solutions.

*Effect of potassium iodide concentration on solution absorbancy*

The molar absorptivity initially increases rather rapidly with increasing iodide concentration (Fig. 6), but reaches a maximum before $SnI_2$ begins to precipitate.

*Effect of stannous chloride concentration on solution absorbancy*

Solution absorbancies increase only slightly with increasing stannous chloride concentration (Fig. 7). The absorbancies, however, were more reproducible if only 2 ml reagent was used.

*Effect of diverse ions, salts, and sulfuric acid on solution absorbancy*

The more common interferences and indications of the extent of their interference are given in Table I. As in all of the stannous halide methods, a separation of iridium from the platinum and other transition metals is necessary. During the reaction period, a small amount of iodine is formed. The table shows that this should not influence the analyses.

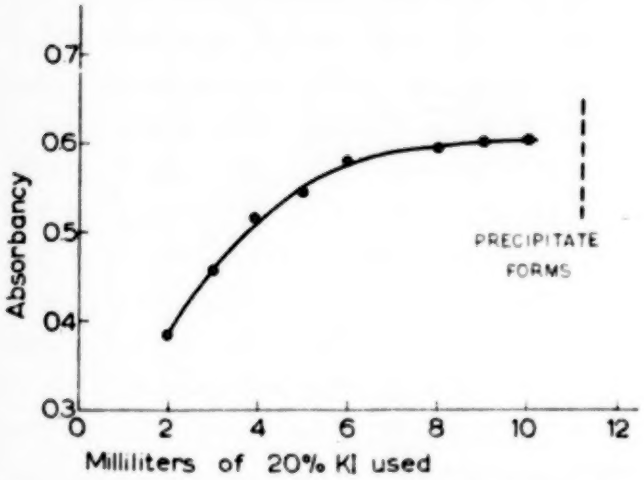

Fig. 6. Effect of amount of KI used on solution absorbancy. 7.7 p.p.m. Ir used in the test solutions. Absorbancy measured at 446 mμ.

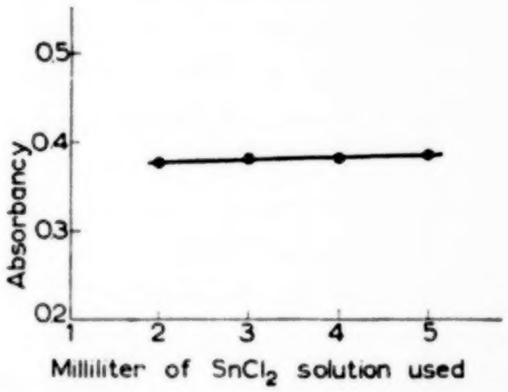

Fig. 7. Effect of amount of $SnCl_2$ used on solution absorbancy. 5.5 p.p.m. Ir used in the test solutions. Absorbancy measured at 446 mμ.

TABLE I

THE CONCENTRATION OF INTERFERENCES NECESSARY TO GIVE A 1% VARIATION IN SAMPLE ABSORBANCY FOR A SAMPLE SOLUTION CONTAINING 4.8 p.p.m. IRIDIUM(III)

| *Interference* | *Concentration (p.p.m.)* | *Direction of change* |
|---|---|---|
| Rh as $RhCl_3$ | 0.02 | + |
| Pt as $PtCl_2$ | 0.09 | + |
| Pd as $PdCl_2$ | — | precipitates |
| Sn as $SnCl_4$ | 70 | + |
| Co as $CoCl_2$ | 13 | + |
| Fe as $FeCl_3$ | 13 | + |
| Sb as $SbCl_3$ | 0.2 | + |
| Ni as $NiCl_2$ | 46 | + |
| Cu as $CuCl_2$ | 23 | + |
| Ti as $TiCl_4$ | 4 | — |
| $Na_2SO_4$ | $4.0 \cdot 10^4$ | — |
| NaCl | $1.2 \cdot 10^4$ | + |
| $I_2$ | 1800 | + |
| Cr as $CrCl_3$ | 27 | + |
| $H_2SO_4$ | $4.9 \cdot 10^3$ | — |

### *Optimum working range*

The Ringbom plot (Fig. 8) shows the working range to be from 0.8 to 11.7 p.p.m. iridium. The system does not obey Beer's law, but is reproducible.

*Precision of method*

Six samples containing 4.9 p.p.m. iridium(III) showed an average deviation of 0.9% and a standard deviation of 1.1%. Another group of six samples containing 6.4 p.p.m. iridium(III) showed an average deviation of 0.9% and a standard deviation of 1.2%.

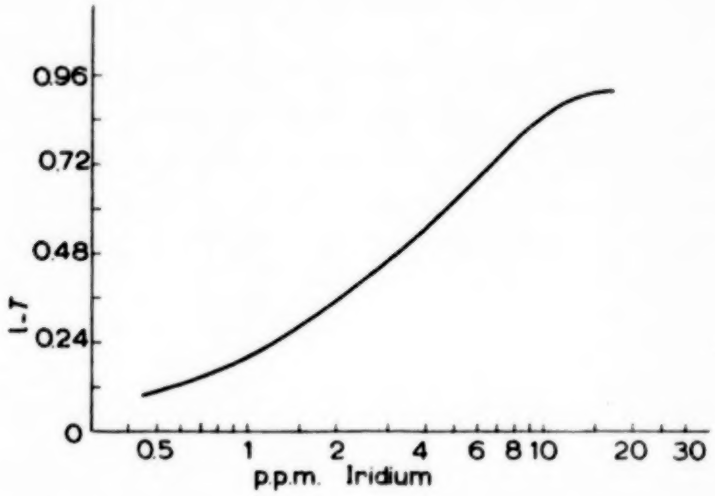

Fig. 8. Ringbom plot of iridium–tin(II) iodide complex determined at 446 mμ.

## DISCUSSION

The need of a simultaneous method of analysis for rhodium and iridium led to the study of the stannous halide reactions. Berman and McBryde[2] failed to simultaneously determine these ions with stannous bromide reagent due to the instability of the rhodium complex. Berman and Ironsides[5] subsequently stabilized the rhodium complex with perchloric acid but reported no work on the simultaneous analysis of rhodium and iridium. An effort was made in the present authors' laboratory to combine and modify the above papers into a simultaneous analysis for rhodium and iridium. The resulting molar absorptivity for the iridium complex was constant over a wider range than that of the unmodified procedure. Both iridium and rhodium singly yielded complexes with molar absorptivities sufficiently stable for our purpose, but in combined solutions the absorbancies were poorly reproducible and accurate only half of the time. Extreme variations often were observed. The perchloric acid that stabilized the rhodium complex made the iridium complex less stable and reproducible, but this did not account for the non-reproducibility of mixed solutions.

The stannous iodide method proved impractical for the simultaneous analysis of rhodium and iridium because of the variation of molar absorptivity with concentration.

The stannous halide reactions were expected to form two homologous series with rhodium and iridium of increasing stability and sensitivity. Maximum absorbancy peaks also were expected to shift toward longer wave lengths in going from chloride to iodide complexes. The reaction with rhodium showed the expected increase in sensitivity but the absorbancy peaks occurred at 475 mμ, 429 mμ, and 460 mμ in going from chloride to iodide reagent. All three solutions were stable over long periods of time if oxidation by light was avoided. With iridium, the sensitivities are of the order: $Br^- > Cl^- > I^-$; the stabilities are of the order: $I^- > Br^- > Cl^-$, again if oxidation by light is avoided. Absorbancy peaks are at 360 mμ for $Cl^-$, 402 mμ for $Br^-$, and 446 mμ for $I^-$. The reaction of the stannous halide reagents with platinum(II) further indicates the failure of the stannous halides to form homologous series of complexes with platinum group metals. The stannous chloride complex has a maximum absorbancy at 403 mμ and a molar absorptivity of $1.5 \cdot 10^4$, the stannous bromide complex has a maximum absorbancy at 463 mμ and a molar absorptivity of $9.3 \cdot 10^3$, but no absorbancy maximum was obtainable with the stannous iodide complex which rapidly increases in molar absorptivity as the wavelength is decreased below 385 mμ. An explanation of the anomalies of the series must await the determination of the structure and mechanism of reaction of the complexes.

The molar absorptivity of the stannous bromide complex of iridium is about three times greater than that for the stannous iodide complex. Working ranges are 0.5–3.0 p.p.m. and 0.8–11.7 p.p.m., respectively. The two methods give similar curves that fail to follow Beer's law; standard and average deviations are also similar —1.2% and 0.9%, respectively. Some advantages of the stannous iodide method are less sensitivity to the matrix acid, the heating period for color development, and sulfuric acid. The complex with stannous bromide also showed a small increase in absorbancy during the first two hours after development, but the major advantage of the stannous iodide method is the use of potassium iodide and hydrochloric acid instead of hydrobromic acid, which requires redistillation and forms a more unstable reagent with stannous chloride than does hydrochloric acid.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial assistance of the Celanese Corporation of America.

## SUMMARY

Iridium ions react with tin(II) iodide reagent to form a stable complex with an absorption maximum at 446 mμ. Beer's law is not obeyed but the reaction is reproducible and the absorbancy is proportional to iridium concentration with an accuracy of ±0.9% over the range 0.8–11.7 p.p.m. Prior separation of iridium from rhodium and other transition metals is necessary. The procedure compares favorably with the tin(II) bromide method. The tin(II) halide reactions with platinum group metals are shown to diverge from true homologous series.

## RÉSUMÉ

L'iridium peut réagir avec l'iodure d'étain(II) pour donner un complexe stable, avec un maximum d'absorption à 446 mμ. Cette réaction permet d'effectuer un dosage spectrophotométrique de cet élément. Une séparation d'avec le rhodium et d'autres métaux de transition est nécessaire.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die spektrophotometrische Bestimmung von Iridium durch Umsetzung mit Zinn(II)-jodid. Platin-und Übergangsmetalle müssen vorher abgetrennt werden.

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# SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

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(Received March 15th, 1961)

## INTRODUCTION

1,2-Diaminocyclohexanetetraacetic acid (Complexone IV) forms very stable complexes with certain metals[1]. Some of the complexes are coloured and consequently complexone IV has been used as the reagent in the photometric analysis of copper[2-4], manganese[5] and iron[6-8]. MARTINEZ AND MENDOZA[9] recommend complexone IV for photometric determination of cobalt. In this method the divalent cobalt complex is oxidised to a violet chelate by hydrogen peroxide in a solution of pH 7.5–9.5. In this alkaline medium, however, several other metals form coloured complexes which will interfere. The present paper describes a similar photometric method for the determination of cobalt using complexone IV in acid solution. In this medium only large amounts of chromium cause interference. The composition and stability of the trivalent cobalt complex have also been determined.

## INSTRUMENTS AND REAGENTS

### *Apparatus*

A Zeiss spectrophotometer Model PMQ II with 1.000- and 5.000-cm glass cells was used for the determination of optical densities. The pH of all solutions was measured with a Beckman Zeromatic pH meter.

### *Reagents*

All chemicals used were of reagent grade except for the 1,2-diaminocyclohexanetetraacetic acid which was a purum product obtained from FLUKA. Stock solutions of cobalt and copper were prepared by dissolving the appropriate amounts of $Co(NO_3)_2 \cdot 6\ H_2O$ and $CuSO_4 \cdot 5\ H_2O$ in water, and standardized by electrolysis. The cobalt and the copper solutions were found to be $1.748 \cdot 10^{-2}$ *M* and $1.76 \cdot 10^{-2}$ *M*, respectively. The complexone IV stock solutions were prepared by dissolving 17.336 g of 1,2-diaminocyclohexanetetraacetic acid and 4 g of sodium hydroxide in water and diluting to 500 ml. The molarity was checked by titration of a standard zinc solution using Eriochrome Black T as indicator and found to be 0.09592 *M*. Less concentrated standard solutions of the reagent were prepared by appropriate dilution. An acetic acid/sodium acetate buffer was prepared by dissolving 54.4 g of $CH_3COONa \cdot 3\ H_2O$ and 23 ml of acetic acid ($d = 1.05$) in distilled water and diluting to 1 l. The pH of this buffer was 4.65.

## EXPERIMENTAL

### *Absorption curves*

MARTINEZ AND MENDOZA[9] prepared the cobalt complex by addition of hydrogen peroxide to solutions of pH 7.5–9.5 containing cobalt ions and excess reagent, and heating the solutions to 40°. Preliminary experiments showed that the colour disappeared slowly if the solutions were heated above this temperature. In acid solutions, however, the colour intensity was independent of the temperature and time of heating. Hence, an acetate buffer seemed to be a more convenient medium for the preparation of the cobalt complex.

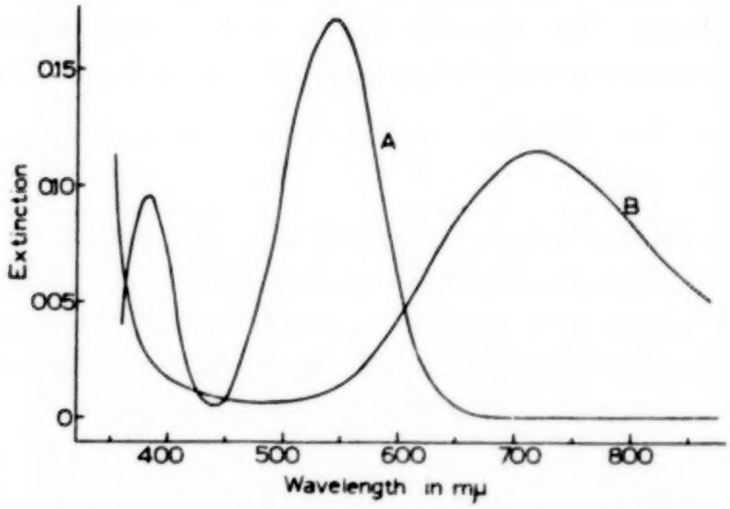

Fig. 1. Absorption curves of trivalent cobalt and copper complexes with complexone IV in acetate buffer of pH 4.65. A: $5.68 \cdot 10^{-4}$ *M* cobalt, B: $1.05 \cdot 10^{-3}$ *M* copper.

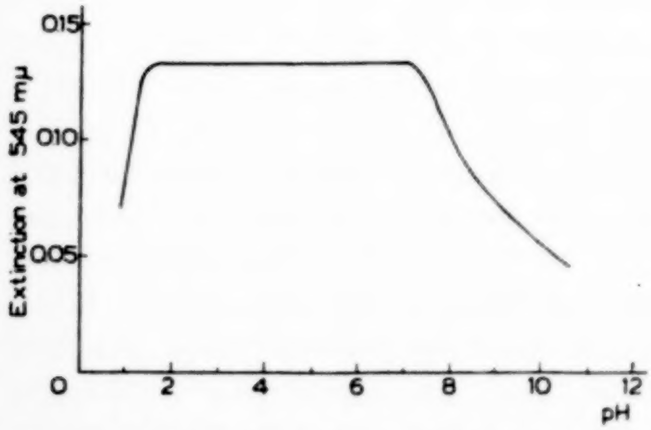

Fig. 2. Effect of pH on the oxidation of the cobalt–complexone IV complex.

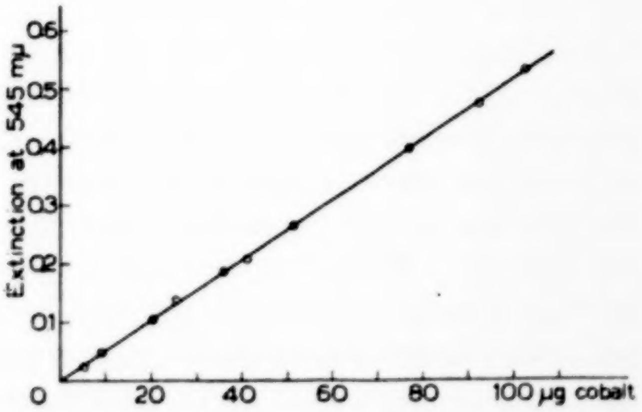

Fig. 3. Standard curve of the cobalt(III)–complexone IV complex measured against distilled water.

An absorption curve of the violet cobalt complex measured against distilled water is plotted in Fig. 1. The solution was prepared by addition of 30% hydrogen peroxide to a buffer of pH 4.65 containing cobalt and excess reagent. The violet colour was developed by boiling the solution gently for 10 min. The curve exhibit maxima at 380 and 545 mμ respectively and the optical densities measured at these maxima were found to be constant for several weeks.

### *Effect of pH*

In order to study the effect of pH on the colour reaction, buffers of different pH were prepared. The same amounts of cobalt, excess reagent and 30% hydrogen peroxide were added to each buffer and the solution was boiled for 10 min. After dilution to constant volume the absorption curves were recorded. Absorption curves obtained from solutions of pH below 9 had distinct maxima at 380 and 545 m$\mu$ respectively. In more alkaline solution the extinction at 545 m$\mu$ decreased with increasing pH. Both maxima disappeared completely at pH 11. The extinction measured at 545 m$\mu$ are plotted against pH in Fig. 2.

The colour intensity had its maximum value in the pH region 1.5 to 7. In this pH range the optical densities were constant, and independent of pH and the time elapsed from mixing the solution. The decrease in the extinctions in alkaline solutions is probably due to decomposition of the reagent during the oxidation with hydrogen peroxide.

### *Beer's law*

For the verification of Beer's law the optical densities were measured for a number of cobalt solutions. The solutions were prepared by addition of 10 ml of the complexone IV stock solution, 5 ml of 30% hydrogen peroxide and different amounts of the standard cobalt solution to 10 ml of acetate buffer. The solutions were boiled gently for 10 min and then diluted to 100 ml. The optical densities at 545 m$\mu$ are plotted against the cobalt concentration in Fig. 3. The system was found to obey Beer's law in the concentration range 1 to 100 $\mu$g of cobalt per ml.

The molar extinction coefficient of the cobalt complex is 305.

### *Interfering ions*

Provided that excess reagent is present colourless ions do not interfere in the determination of cobalt. Ferric iron and manganese which interfere seriously in the alkaline medium recommended by MARTINEZ AND MENDOZA[9], cause no interference when acetate buffer of pH 4.6 is used.

Chromium forms a light green solution with complexone IV which is quantitatively converted to a violet complex when the solution is heated or exposed to the air for some hours. Chromate is reduced to the same violet complex when a solution containing excess reagent is heated with hydrogen peroxide. This violet complex which has a maximum absorption at 540 m$\mu$ and a molar extinction coefficient of about 250 interferes seriously in the determination of cobalt. The interference from small amounts of trivalent chromium can be avoided by measuring the optical density against an aliquot containing exactly the same amount of all ions except hydrogen peroxide. The blank should be boiled gently for 10 min in order to convert the chromium completely to the violet complex.

Nickel and copper form blue coloured complexes with the reagent and they give a small contribution to the optical density at 545 m$\mu$. The absorption curves of these two complexes do not change when the solution is heated or oxidized with hydrogen peroxide. Hence the interference from nickel and copper may be avoided by measuring the absorption against a blank as described above.

The absorption curve of the copper complex is plotted in Fig. 1. The curve has a maximum at 720 m$\mu$ at which wavelength the cobalt complex does not give any absorbance. Measurements of the optical densities of various concentrations of the copper complex showed that Beer's law is obeyed at both 545 and 720 mμ. Thus it is possible to determine the copper concentration by measuring the extinction at 720 mμ and then calculate its contribution to the absorbance at 545 mμ.

In Table I the extinctions measured against distilled water at 720 and 545 mμ of mixtures of copper and cobalt in the presence of excess reagent are reported. The theoretical extinctions and the absorbance of copper at 545 mμ were taken from standard curves. The solutions were prepared by mixing different amounts of copper and cobalt in acetate buffer. Excess reagent and 30% hydrogen peroxide were added and the solutions boiled gently for 10 min. As seen from the Table the concentration of cobalt and copper can be determined in the same solution with an experimental error of 2%.

TABLE I

PHOTOMETRIC DETERMINATION OF COBALT IN PRESENCE OF COPPER

| *Molarity* | *E theoretical* | | *E measured* | | *E of Cu at 545 mμ* | *E of Co at 545 mμ* | *Error %* | |
|---|---|---|---|---|---|---|---|---|
| | *Cu 720 mμ* | *Co 545 mμ* | *720 mμ* | *545 mμ* | | | *Cu* | *Co* |
| $3.50 \cdot 10^{-4}$ Cu<br>$3.50 \cdot 10^{-4}$ Co | 0.192 | 0.520 | 0.194 | 0.529 | 0.019 | 0.510 | +1.0 | −1.9 |
| $5.28 \cdot 10^{-4}$ Cu<br>$3.50 \cdot 10^{-4}$ Co | 0.289 | 0.520 | 0.293 | 0.547 | 0.029 | 0.518 | +1.4 | −0.4 |
| $7.92 \cdot 10^{-4}$ Cu<br>$3.50 \cdot 10^{-4}$ Co | 0.432 | 0.520 | 0.433 | 0.553 | 0.042 | 0.511 | +0.2 | −1.9 |

### *The composition of the cobalt complex*

Martinez and Mendoza[9] suggest that the colour reaction is due to a peroxide complex or, more probably, that cobalt is oxidized to the trivalent state by hydrogen peroxide. They do not, however, give any evidence of the composition or oxidation state of the complex.

Our experiments showed that the colour reaction is independent of the kind of oxidizing agent. The same colour and absorption curve were obtained by heating solutions of the divalent complex with hydrogen peroxide or by addition of lead dioxide or potassium permanganate to the solutions at room temperature. Exactly the same absorption curve was also obtained by anodic oxidation of the divalent complex or by addition of complexone IV to solutions of sodium cobaltinitrite. These experiments indicate that the violet complex consists of complexone IV and cobalt in its trivalent state.

For the evaluation of the composition of the complex Job's method[10] was employed. Different ratios of cobalt and reagent in acetate buffer were oxidized with hydrogen peroxide, and the solutions containing a constant total concentration of reactants were diluted to constant volume. The optical densities at 545 mμ were measured and plotted against the ratio [Co]/[Co] + [R]. A maximum, obtained where the cobalt and the reagent were present in the ratio 1 : 1, indicated the formula Co(III)R. The experiments were repeated using lead dioxide as oxidizing agent and the same maximum corresponding to the ratio 1 : 1 was obtained.

Similar studies using the molar ratio method[11] yielded an identical composition for the complex.

### *The stability of the cobalt(III) complex*

It was not possible to evaluate the stability of the cobalt(III) complex by JOB's method of continuous variation. Some of the reagent was decomposed by the oxidation with hydrogen peroxide leading to low values for the optical densities of solutions containing excess cobalt. An indirect spectrophotometric method described by HUGHES AND MARTELL[12] was, however, found to be useful in the calculation of the stability constant.

The method is based upon the displacement of one ion by another, according to the equilibrium:

$$\mathrm{MR} + \mathrm{M'} \rightleftharpoons \mathrm{M'R} + \mathrm{M}$$

$$K' = \frac{K_{\mathrm{M'R}}}{K_{\mathrm{MR}}} = \frac{[\mathrm{M'R}]\,[\mathrm{M}]}{[\mathrm{MR}]\,[\mathrm{M'}]}$$

where [ ] represent the molar concentrations, R the chelating agent and $K'$ the displacement equilibrium constant. The determination of $K'$, which is equal to the ratio of the stability constants of M'R and MR leads directly to a calculation of the stability constant of one metal chelate (MR) if that of the other (M'R) is known. If both metals form 1 : 1 complexes with the reagent as in the equation above, the exact concentration of the reagent need not be considered. Hence, the method should be applicable to 1 : 1 complexes even if some reagent is decomposed during the preparation of the solutions.

Trivalent cobalt and copper ions form 1 : 1 complexes with complexone IV and as indicated in the preceding section, the concentration of these two chelates can be determined in presence of each other. The stability constant of the copper chelate has been determined previously[1]. Consequently the displacement method can be used in the calculation of the stability of the cobalt(III) complex.

Solutions containing cobalt and a slight excess of reagent were oxidized with hydrogen peroxide following the procedure outlined above. A known amount of copper was then added and the solutions were diluted to constant volume. After two days of standing the absorption of the copper complex at 720 mμ had increased to its maximum value, indicating equilibrium in the displacement reaction, and the optical densities at 545 and 720 mμ were measured. The optical densities were corrected for the absorption of uncomplexed metals as described by HUGHES AND MARTELL[12] and the corresponding concentrations of the two metal complexes (MR and M'R in the equation above) were determined from standard curves. The molar extinction coefficients for uncomplexed metals at the two wave lengths and for the copper complex at 545 mμ were taken from absorption measurements on pure substances. The concentration of uncomplexed metals (M and M') was taken as the difference between the total concentration of the metal species and the concentration of the respective metal complex (MR and M'R)

The displacement equilibrium constant $K'$ was then calculated and $K_{\mathrm{Co(III)R}}$

obtained from the equation $K_{\mathrm{Co(III)R}} = K_{\mathrm{CuR}}/K'$. The results are given in Table II. All measurements were made at 20° in solutions with ionic strength 0.08. A mean value of the stability constant $K_{\mathrm{Co(III)R}} = 8.5 \cdot 10^{21}$ was obtained when the value of log $K_{\mathrm{CuR}}$ was taken equal to 21.30 as determined by SCHWARZENBACH[1].

TABLE II

DETERMINATION OF THE STABILITY CONSTANT OF COBALT(III)–COMPLEXONE IV

| *Total molar concentration × 10⁴* | | *Extinction measured* | | *Molar concentration found × 10⁴* | | | | $\log K_{\mathrm{Co(III)R}}$ |
|---|---|---|---|---|---|---|---|---|
| *Co* | *Cu* | *720 mμ* | *545 mμ* | *CuR* | *Cu(II)* | *Co(III)R* | *Co(III)* | |
| 5.24 | 4.40 | 0.127 | 0.679 | 1.82 | 2.58 | 4.42 | 0.82 | 22.08 |
| 3.52 | 4.37 | 0.093 | 0.404 | 1.26 | 2.27 | 2.68 | 1.69 | 21.76 |
| 6.16 | 5.24 | 0.082 | 0.184 | 0.40 | 5.76 | 1.05 | 4.20 | 21.85 |
| | | | | | | | | Mean 21.9 ± 0.2 |

## ACKNOWLEDGEMENT

The authors are indebted to Prof. HAAKON HARALDSEN for his interest in this investigation and for the facilities placed at their disposal.

## SUMMARY

Cobalt(III) forms a water-soluble complex with complexone IV. The violet complex has an absorbance maximum at 545 mμ and obeys Beer's law from 1 to 100 μg cobalt per ml. The complex is easily prepared and a procedure for the spectrophotometric determination of cobalt in acid medium is given. In this method only large amounts of chromium cause significant interference. The complex contains the cobalt and the reagent in a ratio of 1 : 1, the molar extinction coefficient is 305 and the stability constant of the complex is $8.5 \cdot 10^{21}$.

## RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du cobalt au moyen du complexon IV (acide diamino-1,2-cyclohexanetétracétique), et addition de peroxyde d'hydrogène pour obtenir le complexe violet de cobalt(III), très stable. En milieu acide, seul le chrome en forte concentration peut gêner.

## ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Kobalt mit Komplexon IV und Wasserstoffperoxyd, wobei der sehr stabile, violett gefärbte Kobalt(III) Komplex entsteht. Die Reaktion wird in saurer Lösung ausgeführt, in der nur grössere Mengen Chrom störend wirken.

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# VOLTAMMETRY AT INERT ELECTRODES

## II. CORRELATION OF EXPERIMENTAL RESULTS WITH THEORY FOR VOLTAGE AND CONTROLLED POTENTIAL SCANNING, CONTROLLED POTENTIAL ELECTROLYSIS, AND CHRONOPOTENTIOMETRIC TECHNIQUES. OXIDATION OF FERROCYANIDE AND *o*-DIANISIDINE AT BORON CARBIDE ELECTRODES

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(Received March 18th, 1961)

Data were presented in previous communications[1,2] which demonstrated the analytical utility of boron carbide ($B_4C$, "Norbide", Norton Company, Worcester, Mass.) electrodes. The purpose of the present study is to determine the adherence of experimental data at $B_4C$ electrodes to fundamental current–voltage relationships. Data for these studies were obtained by employing voltage ($E$) and controlled potential ($P$) scanning, constant potential electrolysis, and chronopotentiometry. The equations upon which this work is based are given in Table I. Equations in this table apply only to results obtained under conditions of semi-infinite linear diffusion to a plane electrode, where only one electrode process is possible, and where both oxidized and reduced forms of the electroactive species are soluble in the solution. Conditions under which eqns. (1) and (2) are applicable are restricted further to electrode processes whose rate is mass transport controlled. Constant potential electrolysis, for purposes

TABLE I

EQUATIONS FORMING THE BASIS OF THIS INVESTIGATION

| *Experimental conditions* | *Pertinent equation* | |
|---|---|---|
| Electrode potential varies linearly with time | $i_p = kn^{3/2}v^{1/2}D^{1/2}C^b A$ | (1) |
| Correction of $i_p$ (approx.) for $IR$ drop when *applied voltage* varies linearly with time | $i_{p(\mathrm{true})} = i_{p(\mathrm{exper})}\,(1 + Ri_p/\Delta E)^{1/2}$ | (2) |
| Constant potential electrolysis | $i_t\, t^{1/2} = \dfrac{nFAC^b\, D^{1/2}}{\pi^{1/2}}$ | (3) |
| Constant current electrolysis (chronopotentiometry) | $iT^{1/2} = \dfrac{nFAC^b\, D^{1/2}\,\pi^{1/2}}{2}$ | (4) |

Note: The derivation of these equations and references to the original literature may be found in ref.[12].

of this study, is always carried out at potentials which insure mass transport control. In chronopotentiometry, the process is likewise mass transport controlled at the transition time.

The validity of eqns. (3) and (4) is seemingly well established at conventional electrodes. A number of investigators have verified the dependence of the peak current on some or all of the parameters in eqn. (1) at rapid scan rates, but stringent tests of $i_p$ dependence on all of these parameters have not been reported, to the best of our knowledge, at a given solid electrode for polarization rates below 1 V/min. Since the primary purpose of this study is to demonstrate the behaviour of $B_4C$ electrodes, attempts were made to eliminate uncertainties, experimental or theoretical, which would detract from this goal. A method, which does not depend upon a knowledge of the electrode area, diffusion coefficient, or concentration of electroactive species, is described for the experimental verification of the constant, $k$, in the RANDLES-SEVCIK[3,4] equation for the peak current (eqn. 1). Since eqns. (1), (3), and (4) are based on the same fundamental postulates, it is possible to correlate results obtained by the different techniques and thus arrive at an evaluation of the electrode apart from errors or uncertainties in the postulates or in the absolute values of $C^b$, $D$, or $A$. Since the linear diffusion equations offer the simplest mathematical formulations, this mode of mass transport was chosen for purposes of this investigation.

Demonstration of the internal consistency of the various linear diffusion equations should make it possible to assess the validity of eqn. (1) at slow polarization rates. In this work, the diffusion coefficients given by VON STACKELBERG *et al.*[5] were used. These $D$-values were calculated from eqn. (1). RULFS[6] and MACERO[7] have determined $D$ for $Cd^{+2}$ in 0.1 $M$ KCl by non-electrochemical means. REILLEY *et al.*[8], using chronopotentiometry, have calculated this same $D$. $D^{1/2}$-values for $Cd^{+2}$ determined by these four investigators vary by less than 1% from the mean value and show a maximum spread of 1.9% compared to the lowest value. The value determined by VON STACKELBERG and coworkers is only 0.7% higher than the mean. In a previous communication[2], it was shown that areas of $B_4C$ electrodes calculated on the basis of $D$-values for ferrocyanide (FeoCy) given by VON STACKELBERG *et al.* agree with those calculated on the basis of their $D$-values for ferricyanide within less than 1%, and with projected geometric areas as well as these could be determined. It is assumed, therefore, that it should be possible to determine the absolute validity of eqn. (1) within about ±2% on the basis of present knowledge of $D$-values.

From the values of $k$, the slopes of current–voltage curves and chronopotentiograms, constancy of $E_{1/2}$ with current density and concentration of electroactive species, and the relationship between $E_{p/2}$, $E_{1/2}$, and $E^{\circ\prime}$, certain conclusions are reached concerning the reversibility of the oxidation of FeoCy in KCl solutions at $B_4C$ electrodes. The oxidation of *o*-dianisidine in 1 $M$ $H_2SO_4$ is included to show the applicability of the techniques employed to a reversible, 2-electron process.

The quantities $i_p$ and $(it^{1/2})$ may be related if the potential of the electrode for the determination of the latter quantity is adjusted to a value more cathodic (or more anodic in the case of oxidations) than the potential at which the peak current is measured. Thus, simultaneous solution of eqns. (1) and (3) gives

$$i_p = (it^{1/2}) \frac{(nv\pi)^{1/2}}{F} k \tag{5}$$

If $i_p$ is expressed in $\mu$A, $(it^{1/2})$ in $\mu$A-sec$^{1/2}$, and the expression rearranged, the equation becomes

$$9.45 \cdot \frac{i_p}{(it^{1/2})n^{1/2}} = k \cdot 10^{-5} \quad (6)$$

for scan rates of 200 mV/min.

If the same experimental conditions are used for the determination of $(it^{1/2})$, the corresponding $(iT^{1/2})$ from chronopotentiometric measurement should be

$$(iT^{1/2}) = (it^{1/2}) \frac{\pi}{2} \quad (7)$$

Eqns. (5), (6) and (7) are dimensionally correct.

From eqn. (5) it can be seen that the numerical value of the RANDLES–SEVCIK constant can be determined experimentally without knowledge of $C^b$, $D$, or $A$ when $n$ is known. The value of $k$ at 25° deduced from calculations of RANDLES[3] and NICHOLSON[9] is about $2.72 \cdot 10^5$. MATSUDA AND AYABE[10] calculated 2.69. SEVCIK found 2.17. STREULI AND COOKE[11], using a shielded Hg pool electrode, report values of $k$ in agreement with SEVCIK's value, but their $k$'s required a knowledge of $D$ and an extraneous factor, $m$, which is not defined. DELAHAY[12] has selected the value 2.72 as the more reliable. Constancy of experimental values and comparison with this $k$ should provide a basis for the evaluation of an electrode. Under proper conditions, the oxidation of ferrocyanide on the reduction of ferricyanide in KCl solutions can be used as a reliable test system. If it can be established by independent methods that the electrochemical redox reaction conforms to the conditions for which eqns. (1), (3) and (4) are applicable, the interrelation of data obtained by a scanning technique and that by either controlled potential electrolysis or chronopotentiometry permits the determination of $n$.

### *Shape of the current–voltage curve and relationship between $E_{p/2}$ and $E_{1/2}$*

The shape of the c–V curve ($P$-scan) is determined from the reciprocal slope of a plot of log $[(i_p - i)/i]$ *vs.* $E$. Such a plot is comparable to that of log $[(i_d - i)/i]$ *vs.* $E$ in conventional polarography. The potential at which the log term becomes zero coincides with the potential $E_{p/2}$, and the reciprocal slope for a mass transport controlled process is $0.056/n$V. To date, no such evaluation of the slope is known to exist in the literature, although these conclusions are readily deduced from the work of RANDLES[3]. Since a number of rather vague statements appear in the literature concerning the relationship of $E_{p/2}$ to $E_{1/2}$ (or $E_{1/4}$ in chronopotentiometry) and $E_p$ and concerning the slope of peak-type current–voltage curves a derivation of the slope is given in the Appendix. Reference to the excellent paper of MATSUDA AND AYABE[10] should clarify the potential relationships.

## EXPERIMENTAL

The $B_4C$ electrodes and shields of masking tape for linear diffusion studies were described elsewhere[2]. The same three electrodes were used although the shields were changed as required. Mass transport by semi-infinite linear diffusion was approximated with the shields and checked by performing controlled potential electrolyses on a solution of potassium ferrocyanide in potassium chloride supporting electrolyte. The current–time curves were analyzed for constancy of the product $(it^{1/2})$. If this product was not constant, the electrode was repositioned and another current–time curve recorded. The procedure was repeated until ($it^{1/2}$) was constant for a minimum of 90 sec, a time sufficient to record the c–V curve at 200 mV/min.

Current–voltage curves at stationary electrodes in unstirred solution were recorded using either the Leeds and Northrup Model E Electrochemograph (ECG) or a controlled potential scanning instrument. The controlled potential scanner was based on a circuit published by BOOMAN[13]. The description of a more refined instrument by KELLEY, JONES AND FISHER[14] and a description of the controlled potential technique as applied to dropping mercury polarography has already appeared. The design and operational features of the instrument used in the present work is described elsewhere[15]. This instrument was used also for the controlled potential electrolyses and as a constant current source for chronopotentiometry. The potential–time curves were recorded on a Speedomax G recorder with a chart speed of 8 in./min and a full-scale balance time of 1 sec. An L and N Model 7664 pH Meter was used as a high impedance buffer amplifier in the measurement of electrode potentials. Its output was calibrated against an L and N K-3 potentiometer.

Apparatus for chronopotentiometric studies was conventional. The constant current was known to within 0.1%. Transition times and $E_{T/4}$ values were evaluated by graphic means. To keep the chart reading error less than 1%, transition times were arranged to be at least 6 sec.

Background currents for $E$ and $P$ scanning were determined by recording the c–V curves on solutions of the background electrolyte. The residual current contributions to the peak current ranged from 0.07 to 0.6 $\mu$A on the polished electrode to 0.1 to 0.9 $\mu$A on the rough specimens, the magnitude being dependent upon the supporting electrolyte used. Excellent constancy of the residual current was obtained during the course of a run. The magnitude of the residual current is nearly identical for stationary, shielded electrodes and for unshielded, rotated (>0 to 30 r.p.s.) disc electrodes[16].

All data are reported at 25 ± 0.1°. All potentials are referred to the saturated calomel electrode (S.C.E.) at 25°. Cell resistances were measured with an AC(1000 c.p.s.) conductivity bridge. Cell design, electrode mountings, and additional description of experimental technique may be found in a previous publication[2].

### *Chemicals and reagents*

$K_4Fe(CN)_6 \cdot 3\,H_2O$ and all other inorganic chemicals were Analytical Reagent Grade and used without further purification. The *o*-dianisidine was obtained from E. I. du-Pont de Nemours and Co. through the courtesy of Mr. JOHN TINKER. Polarographic solutions were prepared from aliquots of stock solutions of known concentration or from weighed quantities of the solids dissolved in $N_2$-deaerated, distilled water.

## RESULTS AND DISCUSSION

In order to evaluate the $B_4C$ electrode it was necessary to select a test system whose electrochemical behaviour at solid electrodes was well established. Examination of the literature revealed that the systems most extensively studied were ferrocyanide (FeoCy) and ferricyanide (FeiCy) in KCl. The oxidation of FeoCy or the reduction of FeiCy can involve only one electron, polarographic diffusion coefficients are known[5], both oxidized and reduced forms are soluble, and the electrode reactions take place at potentials where a solid electrode should find its optimum utility. Although less than ideal, the oxydation of FeoCy in KCl solutions was chosen as the basis for the present study.

*Voltage and controlled potential scanning*

The majority of the data on the FeoCy system was obtained by conventional scanning techniques using the Electro-Chemograph. It was deemed advisable, therefore, to ascertain whether or not this data, corrected by means of eqn. (2), was consistent with that obtained by the controlled potential technique. A solution of FeoCy in 1.5 $M$ KCl was prepared by dissolving a few crystals of solid potassium ferrocyanide in the KCl. A single chronopotentiogram was recorded. From the product $iT^{1/2}$, the current range for recording the c–V curve was determined. A polarogram was recorded using conventional ($E$) scanning. The cell circuit resistance was 330 ohm. The polarogram gave an $i_p$ of 128 $\mu$A and an $E_{p/2}$ of $+0.252$ V. Corrected by means of

TABLE II

COMPARISON OF PEAK CURRENTS OBTAINED BY $E$- AND $P$-SCAN

Oxidation of $K_4Fe(CN)_6$ in 1.5 $M$ KCl

| 1<br>$K_4Fe(CN)_6$ conc. · $10^4$ | 2[a]<br>$i_p(\mu A)$<br>$E_{200}$[b] | 3<br>$i_p(\mu A)$<br>$P_{200}$[c] | 4<br>$i_t(\mu A)$<br>Calc. |
|---|---|---|---|
| 2.04 | 6.20 | 5.85 | |
| | 6.24 | 5.75 | |
| | | 6.00 | |
| | | 5.98 | |
| | | 6.00 | |
| | | 6.01 | |
| Mean | 6.22 | 5.93 | 6.34 |
| 4.07 | 13.13 | 11.79 | |
| | 13.20 | 12.87 | |
| | | 12.89 | |
| Mean | 13.16 | 12.52 | 12.65 |
| 6.11 | 20.80 | 20.25 | |
| | 20.55 | 20.28 | |
| Mean | 20.68 | 20.26 | 18.99 |
| 10.18 | 32.92 | 32.55 | |
| | 32.95 | 32.55 | |
| Mean | 32.93$_5$ | 32.55 | 31.64 |
| 20.37 | 64.6 | 64.05 | |
| | 64.5 | 65.05 | |
| | | 64.95 | |
| Mean | 64.65 | 64.68 | 63.31 |
| 46[d] | (145.8) | (146) | 143.00 |

[a] Data in Column 2 corrected for $IR$ drop

[b] Conventional ($E$) scanning on ECG at 200 mV/min

[c] Controlled potential ($P$) scanning at 200 mV/min

[d] See text

eqn. (2), the values were 144 $\mu$A and +0.239 V. A controlled potential scan gave $i_p$ = 144 $\mu$A and an $E_{p/2} = +0.239$ V. The following day the area of the electrode was determined (constant potential electrolysis of 0.2 m*M* FeoCy in 1.5 *M* KCl) to be 0.789 cm$^2$. From eqn. (4) and $iT^{1/2}$, the concentration of FeoCy in the former solution was found to be 4.6 m*M*. These values of $C^b$ and $A$, and $k = 2.72$, $D^{1/2} = 2.51 \cdot 10^{-3}$, $V^{1/2} = 5.77 \cdot 10^{-2}$ were then substituted in eqn. (1). The calculated peak current was 143 $\mu$A. Table II shows results obtained at the same electrode two weeks earlier on solutions of known concentration. The starred entry was calculated on the basis of the entry immediately preceding it in the Table. Values of $i_p$ at $E_{200}$ have been corrected according to eqn. (2). These results indicate that, for concentrations of FeoCy $\geqslant$1.0 m*M*, the agreement between the two methods and with theory is within acceptable limits.

An interesting feature of a comparison of the two scanning techniques is that, for electrode reactions which are not mass transport controlled, much larger discrepancies between the two methods will become evident. The slope of the rising portion of the polarogram will reflect not only the cell resistance but kinetic parameters as well. This information can be used to augment other observations concerning the "polarographic reversibility" of an electrode reaction. Since there are very few reactions which can be studied under conditions such that eqn. (1) applies, considerable care must be exercised when interpreting data obtained by the use of conventional polarographic instrumentation at stationary electrodes in quiet solution.

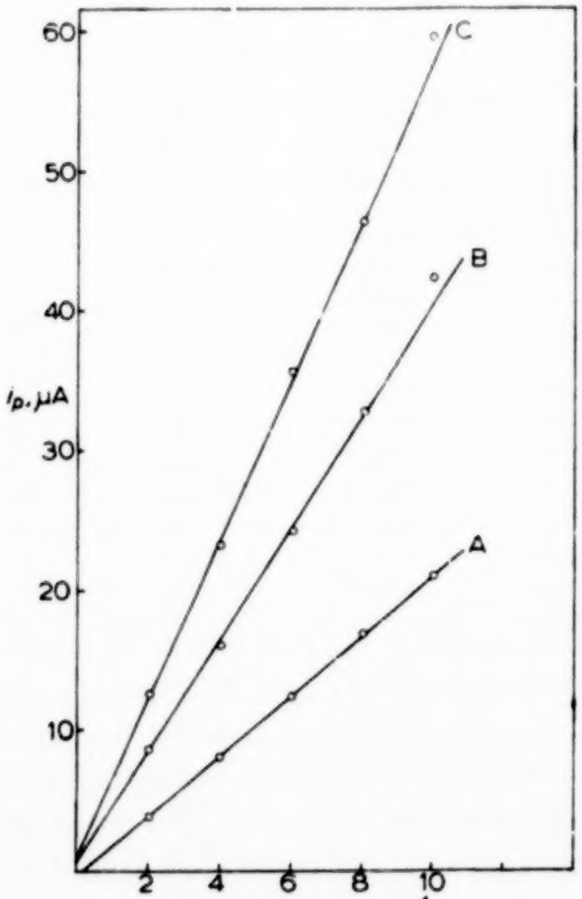

Fig. 1. Variation of $i_p$ with ferrocyanide concentration at three scan rates. Scan rates: (A), 200; (B), 710; (C), 1410 mV/min.

Dependence of $i_p$ on the square root of the polarization rate was verified for scan rates of 200, 700, and 1410 mV/min for the oxidation of 5 concentrations of FeoCy in 0.5 *M* KCl. Peak currents were corrected according to eqn. (2). Fig. 1 is a plot of $i_p$ *vs.* $C^b$ at the three scan rates. The implications of Fig. 1 for practical analysis are clear.

### *Electrolysis at constant potential*

For reasons which will become obvious from later discussion, it is not possible to demonstrate the dependence of $i_p$ on $D^{1/2}$ for the FeoCy–KCl system. The dependence of $it^{1/2}$ on $D^{1/2}$ can be illustrated by data at four KCl concentrations given in Table III. The diffusion coefficients of VON STACKELBERG *et al.* were used to calculate the data in Column 4. The values of $it^{1/2}$ in 0.1 *M* KCl were selected arbitrarily as the basis for the calculations. The largest deviations between observed and calculated values lie within expected limits for this type of comparison[2]. Repetitive determinations of $it^{1/2}$ on the same solution, or on solutions of the same composition at the same electrode, show variations of about 0.5%.

Determination of the product ($it^{1/2}$) at *controlled potential* has shown also that values of this product obtained at constant *applied voltage* reported earlier[1,2] are valid. The peak in the c–V curve for the oxidation of FeoCy occurs well before the onset of the background process. It was therefore possible to use applied voltages of several hundred millivolts more anodic than the peak potential, when necessary, to compensate for *IR* drop when recording the *i–t* curve. For processes which occur close to a second process, the advantages of using controlled potential are readily appreciated.

TABLE III

DEPENDENCE OF ($it^{1/2}$) ON $D^{1/2}$

| 1<br>*KCl conc. moles/l* | 2<br>*$K_4Fe(CN)_6$ conc.·$10^4$* | 3<br>$it^{1/2}$ *Observed* | 4<br>$it^{1/2}$ *Calculated* |
|---|---|---|---|
| 0.1 | 1.0 | 10.10 | — |
| | 10.0 | 105.2 | — |
| 0.5 | 1.0 | 10.43 | 10.02 |
| | 10.0 | 103.8 | 104.4 |
| 1.0 | 1.0 | 10.00 | 9.96 |
| | 10.0 | 106.8 | 103.7 |
| 3.0 | 1.0 | 9.96 | 9.86 |
| | 10.0 | 101.5 | 102.7 |

### *Chronopotentiometry*

Two series of runs were made on the FeoCy–KCl system. In the first series the concentration of KCl was held constant and the FeoCy concentration varied from 0.2 to 4.0 m*M*. Quadruplicate runs (four solutions) were made on the 0.2 and 0.4 m*M*, duplicate runs on the 0.6 and 1.0 m*M*, and single runs on the 2.0, 3.0 and 4.0 m*M* solutions at each current density. In the second series, the concentration of FeoCy was held constant and the KCl concentration varied from 0.05 to 4.0 *M*. In this case

4.0 m*M* FeoCy was used in the 1.0 *M* KCl solution. Results of these runs are given in Tables IV and V.

TABLE IV

$i_0T^{1/2}/C$ *vs.* $C$ AT CONSTANT KCl CONCENTRATION

| $[K_4Fe(CN)_6] \times 10^4$ 1 | $i_0$ 2 | $T$ sec 3 | $i_0T^{1/2}/C$ 4 | $i_0T^{1/2}/C$ Corrected 5 | $i_0T^{1/2}/C$ Mean 6 |
|---|---|---|---|---|---|
| 2.00 | 14.35 | 11.24 | 240.5 | 211.7 | |
| | 17.39 | 8.33 | 251.0 | 217.6 | |
| | 20.29 | 6.08 | 250.2 | 210.8 | |
| | 12.18 | 15.85 | 242.5 | 218.3 | |
| | 8.72 | 27.34 | 227.9 | 209.5 | |
| | 6.10 | 51.48 | 219.0 | 205.6 | 212.3 |
| 4.00 | 30.41 | 12.55 | 240.9 | 213.7 | |
| | 20.29 | 21.46 | 235.0 | 214.2 | |
| | 17.39 | 28.66 | 232.7 | 214.7 | |
| | 14.35 | 40.94 | 229.5 | 214.4 | |
| | 12.17 | 55.51 | 226.7 | 213.7 | 214.1 |
| 6.00 | 40.54 | 12.27 | 236.6 | 213.1 | |
| | 30.40 | 21.30 | 233.9 | 216.1 | |
| | 20.28 | 45.57 | 227.8 | 215.6 | |
| | 17.39 | 59.71 | 224.0 | 213.4 | |
| | 14.35 | 85.73 | 221.3 | 212.4 | |
| | 14.29 | 89.00 | 224.7 | 216.0 | |
| | 12.14 | 119.44 | 221.1 | 213.6 | 214.3 |
| 10.0 | 60.64 | 14.07 | 227.4 | 214.8 | |
| | 40.43 | 30.68 | 223.9 | 214.9 | |
| | 30.33 | 53.07 | 220.9 | 214.4 | |
| | 20.21 | 120.46 | 221.7 | 217.4 | 215.4 |
| 20.0 | 173.2 | 6.53 | 221.3 | 213.2 | |
| | 151.5 | 8.78 | 224.5 | 217.5 | |
| | 134.7 | 11.03 | 223.6 | 217.3 | |
| | 121.2 | 12.91 | 217.8 | 212.0 | |
| | 80.82 | 29.71 | 220.3 | 216.5 | |
| | 40.40 | 113.3 | 215.1 | 213.2 | |
| | 30.30 | 198.4 | 213.3 | 211.8 | |
| | 71.32 | 37.51 | 218.4 | 215.0 | 214.6 |
| 30.0 | 202.0 | 10.81 | 221.4 | 215.5 | |
| | 173.1 | 14.63 | 220.7 | 215.5 | |
| | 151.5 | 18.38 | 216.5 | 212.1 | |
| | 134.7 | 23.63 | 218.2 | 214.2 | |
| | 121.2 | 28.81 | 216.9 | 213.3 | |
| | 80.79 | 63.68 | 214.9 | 212.5 | |
| | 71.28 | 83.63 | 217.3 | 215.2 | 214.1 |
| 40.0 | 303.0 | 8.26 | 217.7 | | |
| | 202.0 | 18.01 | 214.3 | | |
| | 151.5 | 31.73 | 213.3 | | |
| | 134.7 | 40.81 | 215.1 | | |
| | 121.2 | 48.68 | 211.4 | | |
| | 80.79 | 113.56 | 215.3 | | |
| | 71.28 | 145.17 | 214.7 | | 214.5 |

All runs 1.5 *M* KCl, $A = 0.825$ cm², $E_T = +0.44$ V *vs.* S.C.E. Rough electrode. Mean and its standard deviation at 95% conf. level = 214.1 ± 0.33%.

TABLE V

$i_0T^{1/2}/C$ *vs.* KCl CONCENTRATION AT CONSTANT FeoCy CONCENTRATION

| $K_4Fe(CN)_6$ conc. $\cdot 10^3$ 1 | [KCl] moles/l 2 | $i_0$ $\mu A/cm^2$ 3 | T, sec 4 | $i_0T^{1/2}/C$ 5 | $i_0T^{1/2}/C$ corrected 6 | $i_0T^{1/2}/C$ theoretical 7 |
|---|---|---|---|---|---|---|
| 1.00 | 0.05 | 77.52 | 8.47 | 225.6 | 220.8 | |
| | | 55.43 | 16.08 | 222.3 | 218.8 | |
| | | 38.76 | 28.05 | 205.3 | 202.7 | 219.7 |
| 1.00 | 0.10 | 96.90 | 6.14 | 240.3 | 220.2 | |
| | | 77.52 | 9.63 | 240.3 | 224.3 | |
| | | 64.53 | 13.67 | 238.1 | 224.7 | |
| | | 55.43 | 18.26 | 236.7 | 225.1 | |
| | | 38.76 | 36.10 | 232.9 | 224.6 | |
| | | | | Mean | 223.8 | 218.0 |
| 1.00 | 0.20 | 96.90 | 6.14 | 240.3 | 216.5 | |
| | | 77.52 | 9.63 | 240.3 | 221.3 | |
| | | 64.53 | 13.67 | 238.1 | 215.9 | |
| | | 55.43 | 18.18 | 236.7 | 222.9 | |
| | | 38.76 | 35.51 | 231.0 | 221.1 | |
| | | | | Mean | 220.8 | 217.6 |
| 1.00 | 0.30 | 96.90 | 6.3 | 245.2 | 212.4 | |
| | | 77.52 | 9.79 | 242.6 | 216.2 | |
| | | 64.53 | 13.67 | 238.1 | 215.9 | |
| | | 55.43 | 17.87 | 234.5 | 215.0 | |
| | | 38.76 | 35.12 | 229.8 | 215.9 | |
| | | | | Mean | 215.1 | 216.7 |
| 1.00 | 1.5 | 96.90 | 6.52 | 247.1 | 213.5 | |
| | | 77.52 | 10.10 | 246.5 | 219.5 | |
| | | 64.53 | 14.14 | 242.6 | 219.8 | |
| | | 55.43 | 18.64 | 238.9 | 219.0 | |
| | | 38.76 | 36.28 | 233.3 | 219.1 | |
| | | | | Mean | 218.2 | 214.4 |
| 4.00 | 1.0 | 392 | 4.88 | 216.6 | | |
| | | 245 | 12.12 | 213.2 | | |
| | | 196 | 19.11 | 214.2 | 0.397 | |
| | | 98.00 | 74.4 | 211.3 | | |
| | | | | Mean | 213.8 | 214.9 |

$A = 0.516$ cm²; polished electrode

In all solutions except those 4.0 m*M* in FeoCy an increase in $i_0T^{1/2}/C^b$ was observed when the contribution of the background was not taken into account. The observed transition time reflects not only the current consumed by the faradaic process but that used for charging the double layer and, where possible, oxidizing the electrode.

**Bard**[17] has recently pointed out the necessity of considering an equation of the following form

$$\frac{i_0T^{1/2}}{C^b} = \frac{nFD^{1/2}\pi^{1/2}}{2} + \frac{(C_{dl})_{avg.}\Delta E}{C^bT^{1/2}} + \frac{Q_{ox}}{C^bT^{1/2}} \tag{8}$$

If the background process consists in double layer charging only, a plot of $i_0T^{1/2}/C^b$ *vs.* $1/T^{1/2}$ will have a slope of $(C_{dl})$avg $\Delta E/C^b$ with an intercept of $nFD^{1/2}\pi^{1/2}/2$. This plot was made and the corrected values of $i_0T^{1/2}/C^b$ are given in Column 5 in Table IV and Column 6 in Table V. The mean value is 214.1 (Table IV), in good agreement with 214.4 calculated from eqn. (4), and with 214.5, the mean of the data 4.0 m$M$ in FeoCy. The improved constancy of $i_0T^{1/2}/C^b$ with increasing concentration of electroactive species is not peculiar to $B_4C$ electrodes. **Lingane**[18] mentions that best results are obtained in 10 m$M$ solutions. **Bard** used 5 m$M$ solutions at platinum electrodes. **Elving and Smith**[19], using impregnated graphite rod electrodes, also found greatest reproducibility of $iT^{1/2}/C$ for both FeoCy and FeiCy when the concentration of these species was around 1.0 m$M$. Actually, the optimum ratio of concentration to current density will depend mainly upon the roughness of the electrode. For high current densities and low concentrations of electroactive species, the diffusion layer at the transition time will be relatively thin. Since the double layer undoubtedly conforms very closely to the "hills and valleys" on the electrode surface, the capacity of this layer on a rough electrode will be large in comparison to a "smooth" electrode of the same projected area. As the diffusion layer thickness at the transition time increases, the time necessary to charge the double layer is a smaller fraction of the total $T$. Since even electropolished platinum and gold electrodes are not smooth[15], it seems that the establishment of optimum operating conditions must remain somewhat empirical, and be adjusted to the particular solid electrode used.

### *Verification of Randles' constant*

The values of $k$ in eqn. (1), obtained by applying eqn. (5) to data obtained from controlled potential electrolysis at constant potential and by $E$ and $P$ scanning, are listed in Table VI. From this Table it is apparent that agreement between experimental results and eqn. (1) was not achieved for concentrations of KCl $< 0.5$ $M$, but for concentrations $\geqslant 0.5$ the agreement is excellent. The value of 2.72 obtained in

TABLE VI

VARIATION OF THE RANDLES–SEVCIK CONSTANT WITH KCl CONCENTRATION

$K_4Fe(CN)_6$ conc. 2 to $40 \cdot 10^{-4}$ $M$

| *KCl moles/l* | $k \cdot 10^{-5}$ | | |
|---|---|---|---|
| | *E scan* | *either* | *P scan* |
| 0.05 | 1.98 | — | 2.15 |
| 0.10 | 2.06 | — | 2.34 |
| 0.20 | 2.57 | — | 2.52 |
| 0.30 | — | — | 2.62 |
| 0.50 | 2.72 ± 0.02[a] | | |
| >0.50 | | 2.72 ± 0.05[b] | |

[a] Standard deviation of mean, 95% confidence level, 225 determinations of $i_p$

[b] Standard deviation of mean, 95% confidence level, 170 determinations of $i_p$

the 0.5 *M* KCl is the mean of 225 determinations at concentrations of FeoCy ranging from 0.2 to 4.0 m*M*, at three scan rates, using three electrodes, at temperatures ranging from 22.7° to 32.2° (corrected to 25°)[2], with all *E*-scan data corrected according to eqn. (2).

Clearly, the decrease in $k$ with decreasing KCl concentration below 0.5 *M* cannot be the result of changing diffusion coefficients or activity of FeoCy. The ratio $D_{\text{FeiCy}}/D_{\text{FeoCy}}$ increases slightly between 0.05 and 1.0 *M* KCl, but decreases again beyond 1.0 *M*. The change in the ratio never exceeds 2%. The decrease in $k$ from 2.72 to 2.15 amounts to 21%. Changes in activity should be reflected equally in $i_p$ and $(it^{1/2})$. A decrease in $i_p$ with decreasing KCl concentration was noted also by MORRIS AND SCHEMPF[20], but these authors do not discuss its cause.

A slow step in the oxidation of FeoCy at other electrodes has been suggested by several investigators[9,21,22]. Examination of wave shapes, constancy of $E_{1/2}$ with $i_0$ and FeoCy concentration, and of values of $k$ obtained by correcting *E*-scans with those calculated from *P*-scans, should give an indication of the correctness of this assumption.

The inability of eqn. (2) to give values of $k$ which agree with those determined by *P*-scan (Table VI) indicates that the cell resistance is not the only factor contributing to the slope of the rising portion of the c–V curve. Since larger $\Delta E$'s cause the correction to be too small, lower values of $k$ are predicted by eqn. (2). The values of $k$ in 0.2 *M* KCl differ by less than 2% and may merely reflect experimental error. In 0.05 *M* KCl, however, an 8% discrepancy exists which cannot be attributed to this cause.

TABLE VII

VARIATION OF SLOPE OF POLAROGRAM WITH KCl CONCENTRATION

$[K_4Fe(CN)_6]$ constant at $10^{-3}$ *M*

| *[KCl]* | *−1/slope ± 2 mv* |
|---|---|
| 0.05 | 0.066 |
| 0.10 | 0.065 |
| 0.20 | 0.058 |
| 0.30 | 0.059 |
| 0.50 | 0.056 |
| 1.00 | 0.055 |
| 1.5 | 0.057 |
| 2.0 | 0.056 |
| 3.0 | 0.057 |
| 4.0 | 0.054 |

Polished electrode, *P*-scan

Table VII lists data showing the dependence of the reciprocal slope of a plot of log $[(i_p-i)/i]$ *vs.* $E$ on KCl concentration at constant FeoCy concentration. Table VIII shows results of the same plot at constant KCl concentration with varying FeoCy concentration. From Table VII it may be concluded that the reaction did not become mass transport controlled until the KCl concentration reached 0.5 *M*. The data of Table VIII indicates that the slope of the wave is independent of FeoCy concentration at a given KCl concentration. There is no apparent difference between the electrochemical behaviour at a polished or rough electrode. The precision of a single determination at the 95% confidence level was ± 1.5% for the polished electrode and ± 2.4% for the rough electrode for all determinations of $i_p$.

Variation of $E_{p/2}$ with KCl concentration is illustrated in Fig. 2. Values taken from the literature are included in the plot for comparison purposes. Since the equilibrium potential is a function of ionic strength[23], a shift in $E_{p/2} + 0.028$ with KCl concentration is expected. It will be noted, however, that, at low concentrations of KCl the $E_{p/2} + 0.028$ values are removed further from the equilibrium values than are the

TABLE VIII

CONSTANCY OF SLOPE OF POLAROGRAMS AT FIXED KCl CONCENTRATION

| $[K_4Fe(CN)_6] \cdot 10^4$ | $-1/slope$ | $[K_4Fe(CN)_6]$ | $-1/slope$ |
|---|---|---|---|
| *[KCl] constant 1.5 M* | | *[KCl] constant 0.1 M* | |
| 2.0 | 0.053 | 2.0 | 0.066 |
| 6.0 | 0.056 | 4.0 | 0.066 |
| 10.0 | 0.056 | 6.0 | 0.066 |
| 20.0 | 0.056 | 10.0 | 0.067 |

Rough electrode, *P*-scan

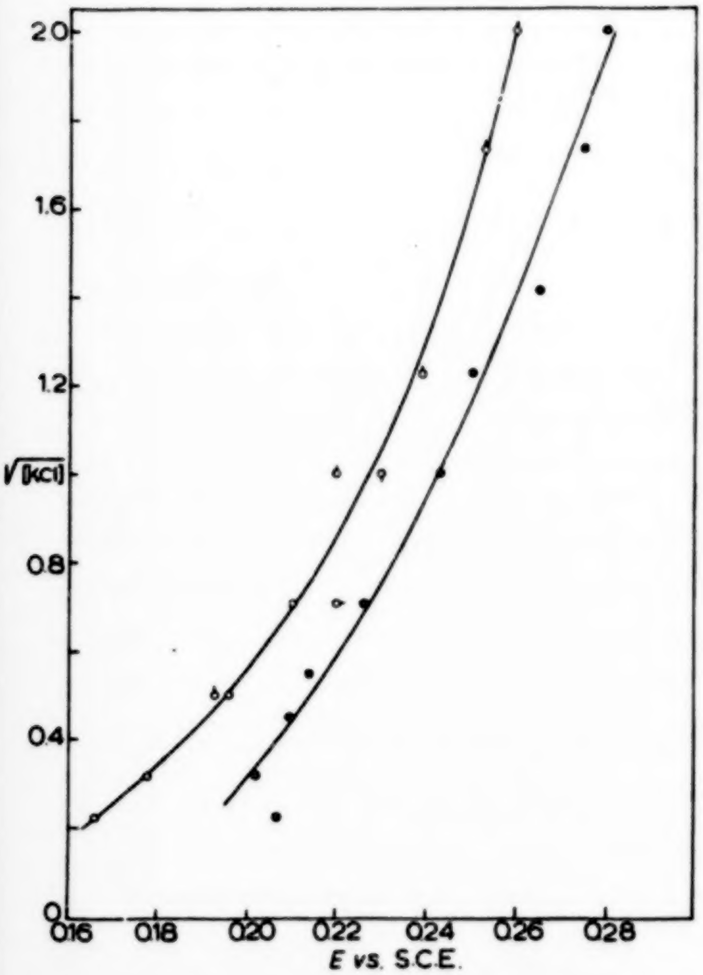

Fig. 2. Variation of $E_{p/2}$ 0.028 V with KCl concentration. (●) Experimental points, mean values; (o) Potentiometric data, Pt electrode[23]; (O-) Potentiometric measurement, graphite electrode[20]; (ϙ) Formal potential, Pt electrode[21]; (ό) Potentiometric data, Pt electrode[24].

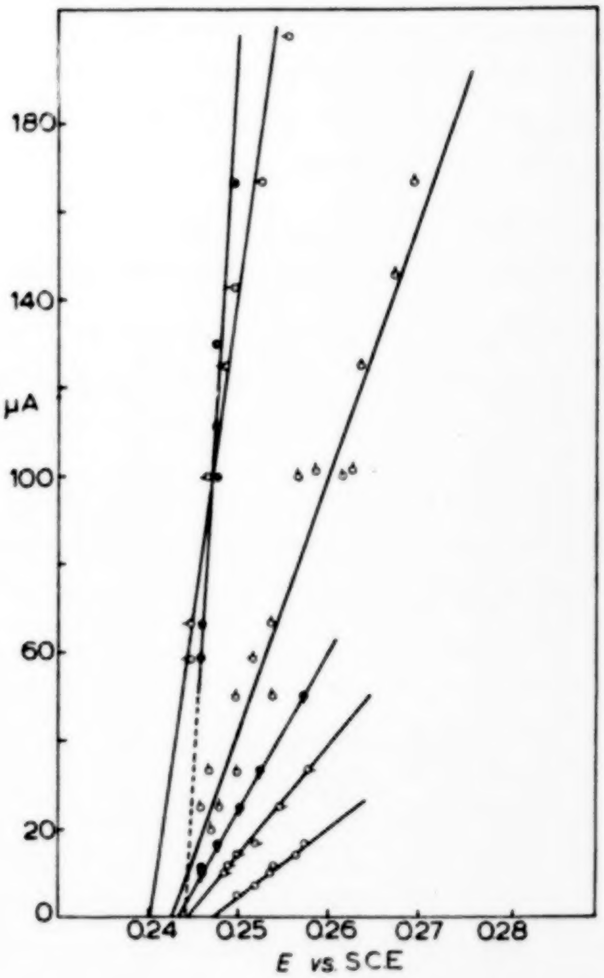

Fig. 3. Variation of $E_{1/2}$ with $i_0$ and ferrocyanide concentration. KCl concentration constant at 1.5 *M*. Ferrocyanide concentration 2 (O), 4 (O-), 6 (ϙ), 10 (ό), 30 (-O), and 40 (●)·$10^{-4}$ *M*.

corresponding potentials at higher concentrations. This shift away from equilibrium is characteristic of charge transfer controlled reactions. In addition, $E_{p/2}$ and $E_p$ were always separated by more than 0.056 V for KCl concentrations $< 0.5$ *M*.

A marked shift in $E_{1/2}$ with $i_0$ and FeoCy concentration (Figs. 3 and 4) is evident also. For a "reversible" process, no shifts are predicted. For a "totally irreversible" process the following equation applies[25]:

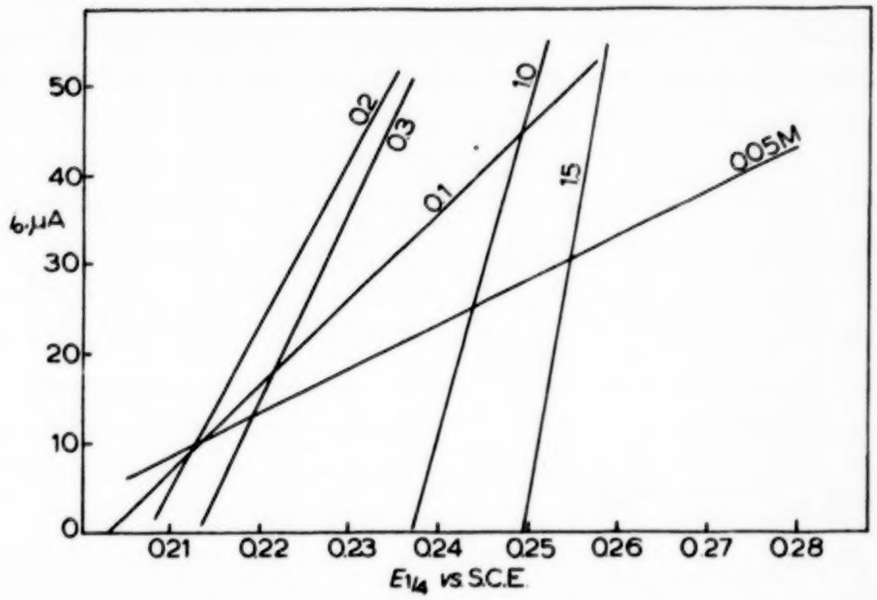

Fig. 4. Variation of $E_{1/2}$ with $i_0$ and KCl concentration. Numbers on lines refer to molar concentrations of KCl. Ferrocyanide concentration $10^{-3}$ *M*.

$$E = \frac{RT}{\alpha_{na}F} \ln \frac{nFC^b k^\circ_{f,h}}{i_0} \quad \frac{RT}{\alpha_{na}F} \ln \left[1 - \left(\frac{t}{T}\right)^{1/2}\right] \tag{9}$$

from which it can be seen that $E$ shifts with both $i_0$ and $C^b$. For processes which proceed at rates such that neither classification is applicable, REINMUTH[26] has shown that a shift of $E$ with these parameters may be expected. Data of Fig. 3 extrapolated

TABLE IX

VARIATION OF SLOPES OF CHRONOPOTENTIOGRAMS WITH $i_0$ AND KCl CONCENTRATION

$K_4Fe(CN)_6$ conc. = $1 \cdot 10^{-3}$ *M*. Polished electrode, $A = 0.516$ cm²

| *[KCl] moles/l* | *−1/slope* | | | | | |
|---|---|---|---|---|---|---|
| | *50 μA* | *40 μA* | *33.3 μA* | *28.6 μA* | *20 μA* | *12 μA* |
| 0.05 | — | 0.080 | — | 0.074 | 0.062 | — |
| 0.1 | 0.081 | 0.080 | 0.063 | 0.070 | 0.062 | — |
| 0.2 | 0.070 | 0.072 | 0.070 | 0.067 | 0.066 | — |
| 0.3 | 0.079 | 0.076 | 0.071 | 0.068 | 0.068 | — |
| 1.0[a] | 0.064$_5$ | — | 0.059 | — | 0.061 | 0.059 |
| 1.5 | 0.074 | 0.070 | 0.075 | 0.069 | 0.067 | — |

[a] $K_4Fe(CN)_6$ conc. = $4 \cdot 10^{-3}$ *M* (actual *i* divided by 4 to fit table)

to $i_0 = 0$ gives values of $E_{1/4}$ in good agreement with the value $E_{p/2} + 0.028$ V from *E*- or *P*-scan curves. Attention is called to the fact that the voltage axis of Fig. 3 is divided into units of only 10 mV. Experimental points have been deleted from Fig. 4 to avoid confusion.

Finally, Table IX shows the values for the reciprocal slopes of plots of log $(T^{1/2} - t^{1/2})/t^{1/2}$ *vs.* $E$ for 1.0 m*M* FeoCy in several concentrations of KCl. Mass transport control of the reaction is indicated for high concentrations of both FeoCy and KCl at low current densities only.

Consideration of the data obtained by the several techniques described indicates that the oxidation of FeoCy in KCl at $B_4C$ electrodes involves a slow electron transfer step. The charge transfer step is rapid enough, however, so that, at slow polarization rates or low current densities, diffusion becomes the rate-determining process in high concentrations of KCl (*E*- or *P*-scan) and high FeoCy concentrations (chronopotentiometry). From chemical considerations, it is difficult to see, however, why this system should show such abrupt departure from reversible behaviour. It is possible that many of the effects of varying KCl concentration could be explained on the basis of changes in double layer structure. The present investigation was carried out primarily to demonstrate the acceptability of $B_4C$ electrodes for electrochemical investigations rather than for the elucidation of any specific reaction mechanism, and further study of the FeoCy oxidation is necessary to establish the validity of either explanation.

The data presented in this section represents about 900 determinations collected in a period of 1½ years. The self-consistency of the data attests to the long-range reproducibility of $B_4C$ electrodes and to their applicability in electrochemical investigations.

### *o-Dianisidine*

The oxidation of *o*-dianisidine in 1 *M* sulfuric acid was carried out at rough and polished $B_4C$ electrodes, at a large platinum foil, and at an electropolished platinum microelectrode[15] by the chronopotentiometric method. At the rough $B_4C$ and platinum foil electrodes, $E_{1/2}$ values were $+0.594$ and $0.592 \pm 0.002$ V, respectively. At both polished electrodes a decrease in $i_0T^{1/2}$ with increasing $i_0$ was noted, but $E_{1/2}$ values at the same $i_0$ were identical at the two electrodes. Reciprocal slopes of plots of log $(T^{1/2} - t^{1/2})/t^{1/2}$ *vs.* $E$ were $-0.029 \pm 0.001_5$ V at the rough $B_4C$ and platinum foil electrodes and $-0.036$ at both polished electrodes. *E*- and *P*-scans at both $B_4C$ electrodes gave values of the RANDLES' constant, $k$, between 2.69 and $2.72 \cdot 10^5$ for $n = 2$. Reciprocal slopes of the plot of log $[(i_p - i)/i]$ *vs.* $E$ were $-0.0275 \pm 0.001_5$ V. The relationship, $E_{p/2} + 0.028 \text{ V} = E_p$ held within $\pm 0.002$ V. Values of $(it^{1/2})$ and $iT^{1/2}$ for values of $iT^{1/2}$ extrapolated to $i = 0$ agreed with eqn. (7) within 1.5%. The data were taken from two series of runs performed one year apart. Mean values of $i_p/C^bA$ were identical for the two series at $B_4C$ electrodes. The oxidation of *o*-dianisidine in 1 *M* sulfuric acid appears to be mass transport controlled when studied at stationary electrodes at slow scan rates.

Further study of the electrochemical behaviour of *o*-dianisidine in 1 *M* sulfuric acid would be of interest. The compound appears to be quite stable in storage, and precision obtained with this compound exceeds that realized with any other electroactive species studied at $B_4C$. Perhaps this system could be used for evaluation studies in preference to the more troublesome FeoCy–KCl or FeiCy–KCl systems.

## APPENDIX

Substituting the symbols defined previously and $A$ — $4\pi v^{2/3}t^{2/3}$ in RANDLES' eqns. (8) and (9)[3], the following relationships for the instantaneous and peak currents are obtained:

$$i_t = \frac{FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3} \delta C_0 \tag{A 1}$$

and

$$i_p = \frac{0.310 FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3} \tag{A 2}$$

Let

$$K = \frac{FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3}. \tag{A 3}$$

Eqns. (A 1) and (A 2) then reduce to the form

$$i_t = K\delta C_0 \tag{A1'}$$

and

$$i_p = 0.0310K \tag{A2'}$$

Then

$$\frac{i_p - i}{i} = \frac{0.310K - K\delta C_0}{K\delta C_0} = \frac{0.310 - \delta C_0}{\delta C_0} \tag{A 4}$$

When the logarithm of eqn. (A 4) becomes zero, solution of this equation for $\delta C_0$ gives, $\delta C_0 = 0.155$. The abscissa (voltage coordinate) corresponding to this value of $\delta C_0$ is determined from Fig. 3 (RANDLES). It is noted that the value of the abscissa so located and the value of the abscissa corresponding to $E_p$ ($\delta C_0 = 0.310$) are symmetric about the origin, $E_{1/2}$. The dimensionless abscissa of RANDLES converted to V gives, for $E_p$ and $E_{p/2}$, the value $0.028\ n \pm E_{1/2}$ V. The plus sign indicates an oxidation and the minus sign a reduction. The observation concerning the peak potential has already been made by DELAHAY[12]. Since $(i_p - i)/i$ also corresponds to $0.310/2$, the value at half peak current, $E_{p/2} \pm 0.028/n = E_{1/2}$. Thus, the potential at half peak current has thermodynamic significance and is directly related to $E_{1/2}$ in conventional polarography.

Application of eqn. (A 4) for other points along the c–V curve *in the vicinity of* $E_{p/2}$ shows that, for a change of 1 unit in the logarithmic term, the voltage increment is between 0.056 and 0.057 V for a 1-electron process. A plot of log $[(i_p - i)/i]$ *vs.* $E$, therefore, should yield a reciprocal slope of about $0.056/n$ V, and the potential at which the logarithmic term becomes zero should be the half-peak potential.

It is advantageous experimentally to be able to attach significance to $E_{p/2}$ in that measurement of $E_p$ is difficult. Due to rounding of the c–V curve in the vicinity of the peak, peak potentials cannot be measured with the same accuracy or precision that is possible for $E_{p/2}$. It may also be concluded that, for a "polarographically reversible" redox reaction, $E_{p/2(\text{cathodic})}$ and $E_{p/2(\text{anodic})}$ will be separated by $0.056/n$V.

## ACKNOWLEDGEMENT

This work was supported by the Atomic Energy Commission through contract AT (11-1)-686, and this support is gratefully acknowledged.

## SUMMARY

An exhaustive study of linear diffusion techniques has been carried out at $B_4C$ electrodes. In addition to proving the utility of $B_4C$ electrodes for both practical and theoretical investigations, some novel inter-relationships between modern electrochemical techniques have been developed, and the validity of the Randles–Sevcik equation has been established for slow scan rates.

## RÉSUMÉ

Les auteurs ont effectué une étude sur l'utilisation d'électrodes inertes de carbure de bore, en voltammétrie. Ils ont examiné en particulier l'oxydation du ferrocyanure et de l'*o*-dianisidine.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung von $B_4C$ Elektroden bei chronopotentiometrischen Methoden. Die Eignung dieser Elektroden für elektrochemische Untersuchungen wurde durch das Studium der Oxydation von Ferrocyanid und *o*-Dianisidin nachgewiesen.

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# SÉPARATION PAR VOLATILISATION DES RADIOISOTOPES DE MERCURE, DE PLATINE, D'IRIDIUM, D'OSMIUM ET DE RHÉNIUM FORMÉS PAR SPALLATION DANS UNE CIBLE D'OR

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(Reçu le 13 mars, 1961)

Dans le cadre de l'étude des réactions de spallation en cours à l'Institut du Radium, nous nous sommes intéressés à la séparation des isotopes de mercure, de platine, d'iridium, d'osmium et de rhénium formés dans des cibles d'or irradiées par des protons de 150 MeV au synchrocyclotron du Laboratoire Joliot-Curie à Orsay. La séparation de ce groupe d'éléments, soit par réactions de précipitation, soit par extraction par solvants, est assez délicate et le traitement d'une cible généralement laborieux. POFFE *et al.*[1] ont séparé le mercure formé dans ces cibles par distillation sous vide. Cela nous a incités à rechercher une méthode plus générale de séparation par volatilisation permettant d'isoler également les autres radioéléments formés en mettant à profit les résultats de recherches effectuées par l'un de nous[2] sur la vaporisation des chlorures d'or.

Le procédé que nous proposons consiste en un fractionnement des éléments ou de leurs chlorures, par sublimation et condensation dans un tube le long duquel est établi un gradient de température. Des procédés analogues ont été utilisés par plusieurs auteurs[3-9] pour purifier ou séparer principalement des composés organiques, soit sous vide, soit en atmosphère contrôlée.

Les feuilles d'or irradiées sont placées au point le plus chaud d'un tube de pyrex ou de quartz. Le tube est traversé, selon le cas, par un courant d'argon, d'oxygène ou de chlore. En chauffant l'or vers 700°, dans l'argon, le mercure distille et se condense dans le tube à une distance bien déterminée. A 270°, dans un courant de chlore, l'or et aussi l'osmium et le rhénium sont transformés en chlorures volatils qui se séparent dans le tube dans l'ordre de leurs températures de condensation décroissantes. En élevant ensuite lentement la température du four on isole les chlorures d'autres éléments, notamment de platine, d'iridium et de tungstène.

## TECHNIQUES EXPÉRIMENTALES

### *Appareillage*

Un tube en cuivre de 90 cm de longueur, 15 mm de diamètre extérieur, 5 mm de diamètre intérieur, est chauffé à une des extrémités par un four électrique de 500 W, et refroidi à l'autre extrémité par un serpentin de cuivre parcouru par un courant d'eau à 10° (Fig. 1). La partie centrale est calorifugée par une couche de 5 cm d'épaisseur de terre d'infusoires. On introduit dans l'âme du tube de cuivre un tube de pyrex ou de quartz d'un mètre de longueur, de 4 mm de diamètre extérieur et de 2 mm de diamètre intérieur dont une extrémité coudée en forme d'U plonge dans un mélange réfrigérant glace-chlorure de sodium (—15° environ). Le tube de pyrex ou de quartz est parcouru, du point chaud vers le point froid, par un courant d'argon, d'oxygène ou de chlore soigneusement desséché, dont le débit est de 0.2 ml/sec à la pression atmosphérique. À la sortie de l'appareil, le gaz est envoyé successivement dans deux flacons laveurs à HCl concentré puis dans un flacon laveur à $HNO_3$ concentré, et ensuite évacué à l'extérieur du laboratoire.

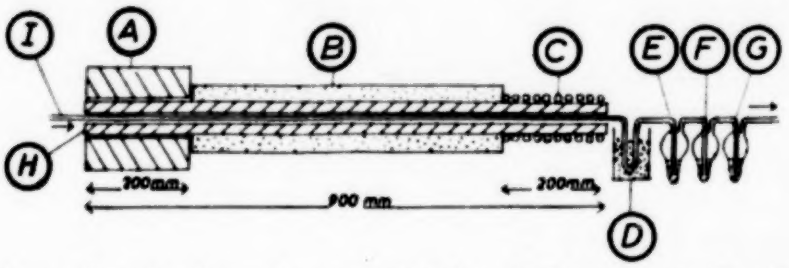

Fig. 1. A, four électrique; B, calorifuge; C, serpentin de refroidissement; D, piège à glace + NaCl; E et F, flacons laveur à HCl conc.; G, flacon laveur à $HNO_3$ conc; H, tube de cuivre; I, tube de pyrex ou de quartz.

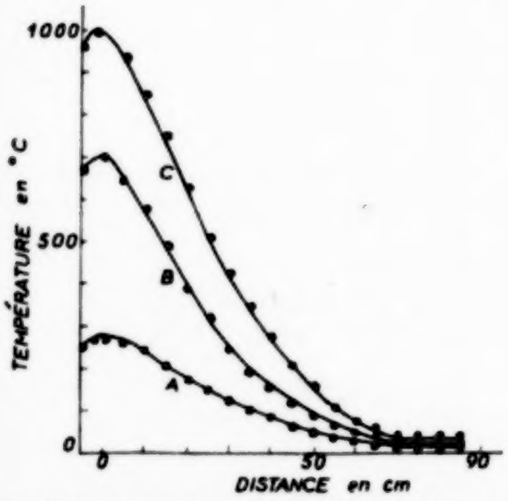

Fig. 2. Variation de la température le long du tube. Températures du four: 270° (courbe A), 700° (courbe B), 1000° (courbe C).

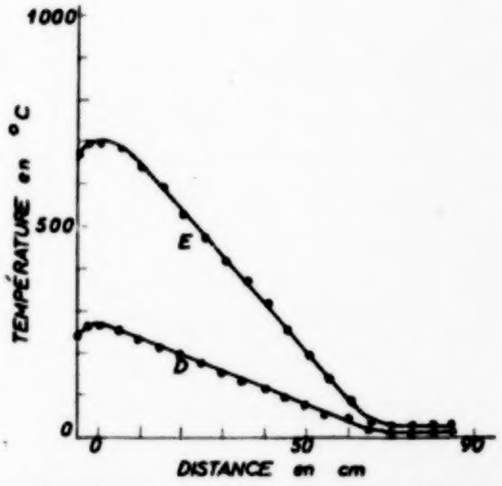

Fig. 3. Gradients de température réalisés avec l'adjonction d'un four auxiliaire au centre du tube.

La température à l'intérieur du tube de cuivre a été mesurée cm par cm à l'aide d'un thermocouple. La température du four étant fixée à 270°, puis à 700° et 1000°, on obtient les trois courbes de température A, B, C (Fig. 2), le point le plus chaud du tube étant pris comme origine des distances. On peut améliorer la linéarité des courbes de température en chauffant légèrement le centre du tube sur 30 cm environ de longueur avec un four auxiliaire (courbes de la Fig. 3). Les températures à l'intérieur du tube sont peu modifiées par la circulation d'un gaz à faible vitesse.

Un dispositif automatique permet de faire monter graduellement la température du four en plusieurs heures jusqu'à une valeur limite prédéterminée.

### *Traitement des cibles d'or irradiées*

*Séparation dans un courant d'argon ou d'oxygène.* La feuille d'or (15 × 10 × 0.01 mm) irradiée par les protons est roulée en cylindre et introduite dans le tube de pyrex froid, à l'endroit défini par le maximum des courbes de température de la Fig. 3.

Le balayage du tube par le courant d'argon ou d'oxygène est établi, puis le four est porté à 700°. Cette température est maintenue pendant 2 à 5 h pour volatiliser le mercure.

*Séparation dans un courant de chlore.* Après distillation du mercure, la feuille d'or roulée est placée dans un deuxième tube de pyrex ou de quartz, et le courant de chlore établi. La température du four est fixée alors à 270°, température qui semble la plus favorable à la volatilisation de l'or à l'état de trichlorure.

La chloruration de l'or est complète après 2 à 6 h de chauffage suivant la quantité de métal présente. Les chlorures d'osmium et de rhénium sont aussi distillés dans ces conditions.

D'autres chlorures peuvent être séparés en élevant lentement la température du four jusqu'à 700° en 5 h pour les tubes de pyrex, ou jusqu'à 1000° en 8 h pour les tubes de quartz.

### *Localisation des produits séparés*

Les tubes de verre ou de quartz sont retirés de la gaine de cuivre et découpés en fragments de 1 cm de longueur dont l'activité est mesurée avec un ensemble de comptage à scintillation muni d'un cristal à cavité, d'iodure de sodium activé au thallium de 5 cm × 5 cm. On porte sur un graphique, en fonction de la distance du point le plus chaud, l'activité de chaque portion du tube dont on peut, en se reportant à la Fig. 2, connaître approximativement la température. La courbe ainsi obtenue présente un certain nombre de pics. L'analyse à l'aide d'un compteur à scintillation associé à un sélecteur d'énergie, du rayonnement $\gamma$ correspondant à chacun de ces pics, et éventuellement la mesure de la période de décroissance de l'activité, permettent de caractériser les éléments séparés. En effet parmi les nucléides formés par spallation de l'or certains, tels que $^{195}$Hg, $^{195}$Au, $^{196}$Au, $^{188}$Pt, $^{189}$Ir, $^{190}$Ir, $^{192}$Ir, $^{185}$Os et $^{183}$Re sont aisément identifiables par la forme de leur spectre $\gamma$. Notons que l'or est en quantité suffisante pour être décelé visuellement.

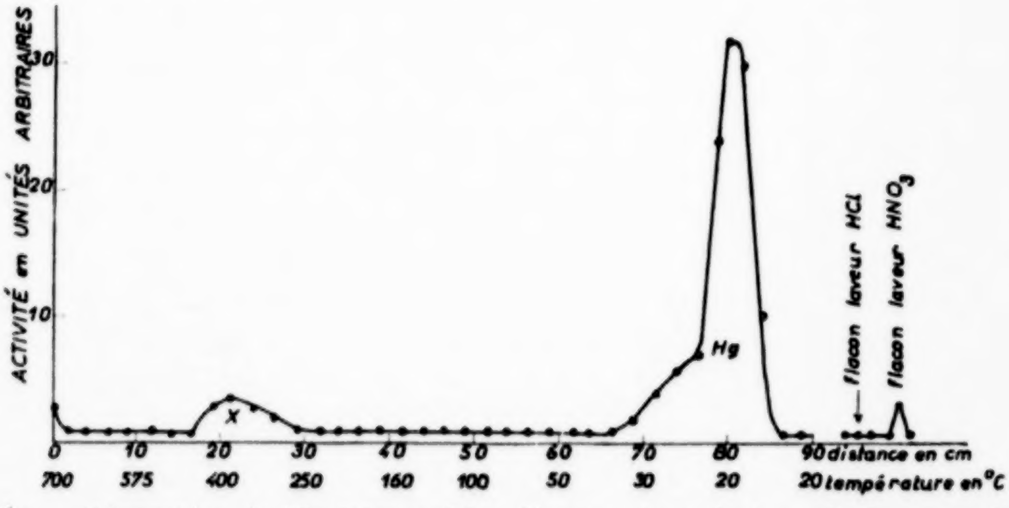

Fig. 4. Séparation de Hg (atmosphère d'argon, température du four: 700°).

## RÉSULTATS EXPÉRIMENTAUX

### *Séparation en atmosphère d'argon ou d'oxygène*

La courbe de la Fig. 4 indique la distribution de l'activité le long du tube obtenue en chauffant à 700° la cible d'or irradiée dans un courant d'argon purifié. Elle fait apparaître un dépôt bien délimité de mercure à environ 80 cm de la feuille d'or. La proportion de mercure extraite en deux heures est voisine de 90%; elle atteint 98% après 5 h de chauffage. Ces rendements sont voisins de ceux obtenus par BEYDON *et al.*[10] en chauffant une cible d'or à 900° sous vide.

Un radioélément en quantité trop faible pour pouvoir être identifié (période d'environ 80 jours) se dépose à une vingtaine de cm du point le plus chaud; on recueille également une activité très faible, décroissant avec une période voisine de 200 jours, dans le flacon laveur contenant $HNO_3$.

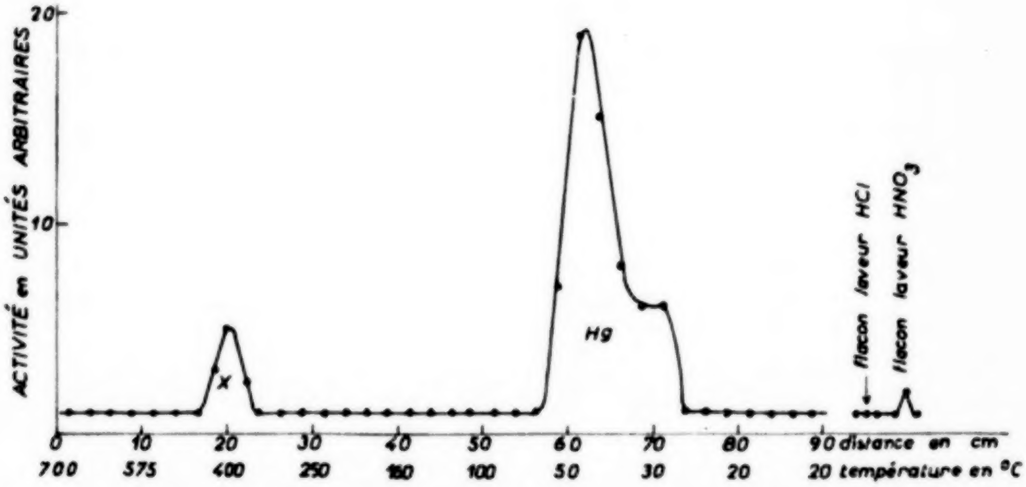

Fig. 5. Séparation de Hg (atmosphère d'oxygène, température du four: 700°).

Si l'on remplace le courant d'argon par un courant d'oxygène, le mercure est extrait de la feuille d'or comme précédemment, mais l'activité déposée avant le mercure est plus importante. Cela n'altère d'ailleurs pas la pureté du mercure qui est bien séparé comme le montre la courbe de la Fig. 5.

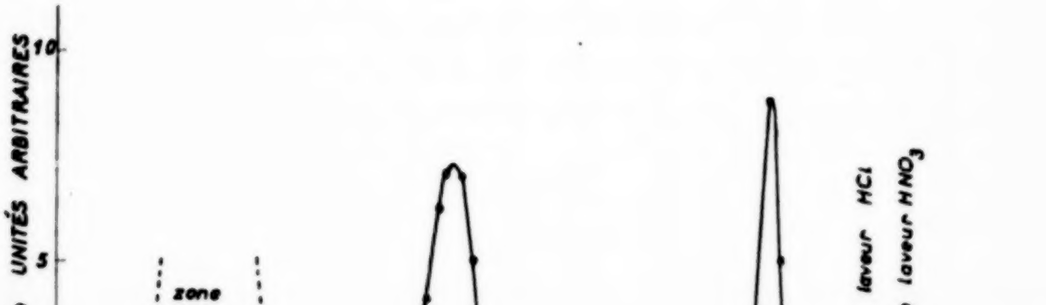

Fig. 6. Séparation de Os et Re (atmosphère de chlore, température du four: 270°).

*Séparation en atmosphère de chlore*

*Expériences à 270°.* L'or, l'osmium et le rhénium donnent des chlorures qui sont volatilisés et bien séparés (Fig. 6).

Le dépôt d'or sous forme de chlorure rouge cristallisé commence à une dizaine de cm du point le plus chaud du tube, et s'étale sur une longueur de 15 à 20 cm. Le tétrachlorure d'osmium, $OsCl_4$, formé se dépose à environ 50 cm. Une petite fraction d'osmium de l'ordre de quelques pourcents est recueillie dans le flacon laveur à HCl, vraisemblablement à l'état de $OsO_4$. Cette fraction est plus importante si l'on n'a pas éliminé toute trace d'oxygène par un chauffage suffisant de la feuille d'or dans un courant d'argon avant d'admettre le chlore dans le tube.

Enfin, on retrouve le rhénium à 80–85 cm du point de départ, soit dans une zone où la température est d'environ 15°. Il est probablement volatilisé à l'état de $ReCl_6$ dont le point d'ébullition est inférieur à 40°.

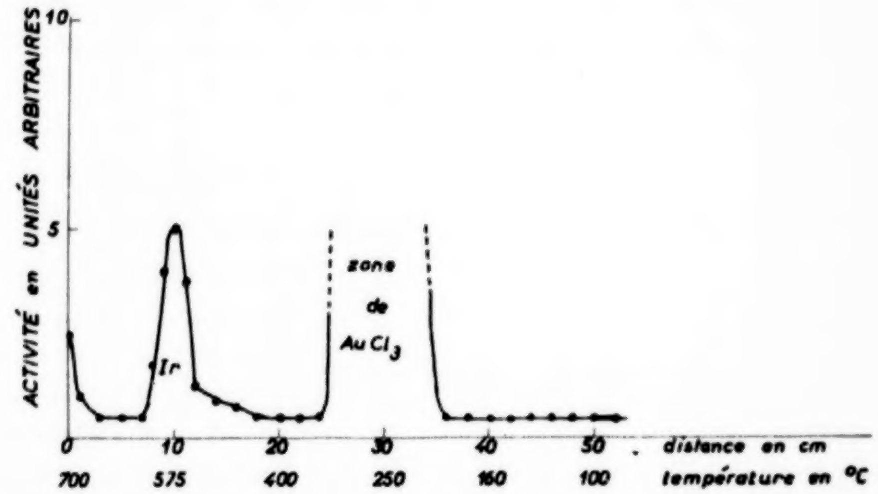

Fig. 7. Séparation de Ir (atmosphère de chlore, température du four: 700°).

*Expériences à 700° et à 1000°.* Après avoir effectué la chloruration de l'or à 270° comme il vient d'être indiqué ci-dessus, la température du four est portée à 700°. Dans ces conditions le chlorure d'or se déplace et se localise dans la portion du tube située à 25–35 cm environ de l'extrémité chaude du tube. L'iridium, alors volatilisé, est bien isolé à une dizaine de cm de l'origine. Quant au platine, il reste au point de départ, vraisemblablement sous forme de $PtCl_2$ (Fig. 7).

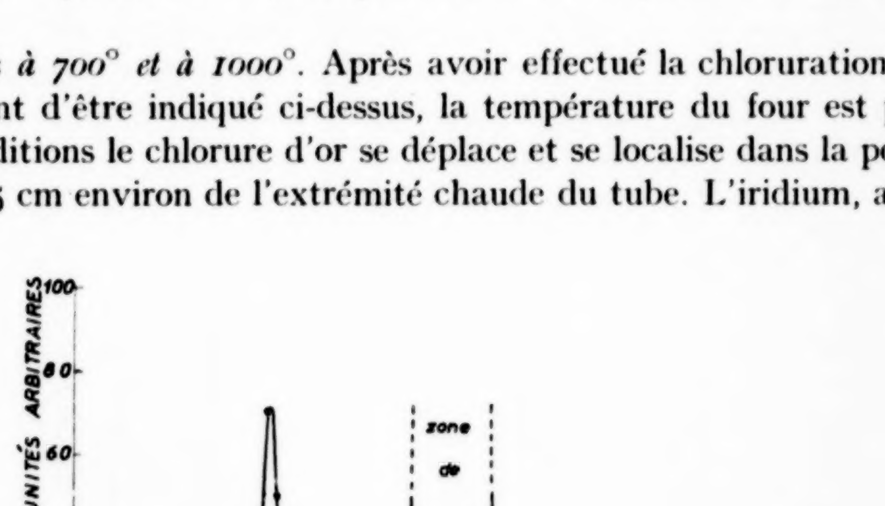

Fig. 8. Séparation de Pt et Ir (atmosphère de chlore, température du four: 1000°).

Par contre, si la température du four est élevée progressivement de 270 à 1000° il se forme $PtCl_4$ qui est volatilisé et se condense à une distance d'environ 40 cm du point chaud, tandis que l'iridium migre à 23-24 cm. L'or migre aussi mais cependant pas suffisamment pour être séparé complètement du platine (Fig. 8). On pourrait remédier à cet inconvénient en chassant assez loin $AuCl_3$ avant de volatiliser le platine. Il suffirait pour cela de déplacer lentement dans la gaine de cuivre le tube de quartz vers la zone chaude, le four étant maintenu à 270°; puis, après une migration suffisante de $AuCl_3$, de replacer le tube à sa position initiale avant d'élever la température du four de 270° à 1000°.

Il nous a paru utile de compléter ce travail par l'étude de la séparation Au, Pt, Ir et W, car il serait également intéressant de rechercher les isotopes de W éventuellement formés par spallation de l'or. Pour faciliter la mise au point de cette séparation, nous avons opéré sur un mélange des métaux: or (une feuille de 15 × 10 × 0.01 mm), platine et tungstène (0.1 mg environ). Les échantillons de platine et de tungstène avaient été auparavant irradiés à la pile. Le platine était ainsi marqué par $^{188}$Pt, et le tungstène par $^{185}$W. Une impureté d'iridium dans le platine a pu être décelée par l'activité de $^{192}$Ir. La Fig. 9 montre que le tungstène est bien séparé de l'or, du platine et de l'iridium. Il se dépose à environ 60 cm de la position initiale, sous forme de cristaux rouges, $WOCl_4$, formés en présence des traces d'oxygène contenues dans le chlore.

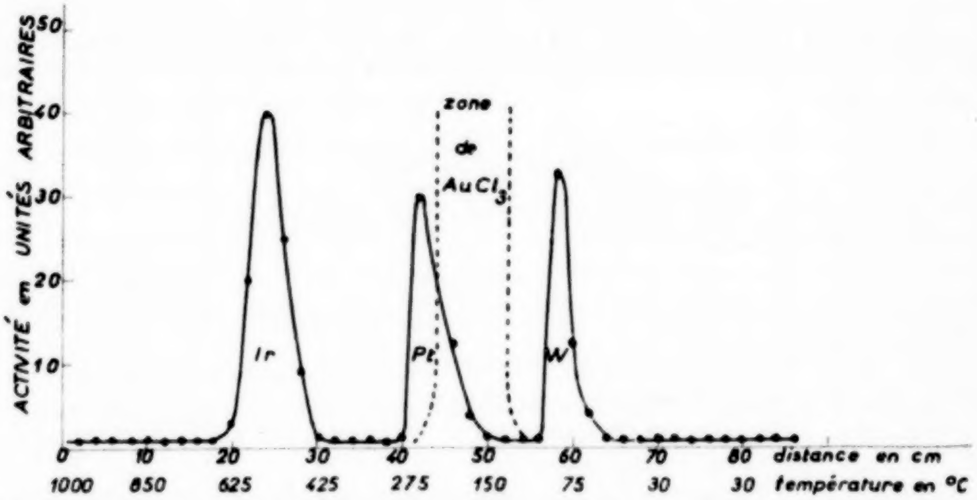

Fig. 9. Séparation de Pt, Ir et W (atmosphère de chlore, température du four: 1000°).

## CONCLUSION

La séparation des isotopes radioactifs de Hg, Pt, Ir, Os et Re formés dans une cible d'or par spallation a été réalisée par volatilisation dans un tube le long duquel est établi un gradient de température. La méthode mise en oeuvre apparaît bien adaptée à la séparation et à la purification de certains radioéléments en quantités impondérables; elle ne nécessite pas l'emploi d'entraîneurs, ce qui pour certains travaux est très important. Son application à divers problèmes de radiochimie est en cours.

## REMERCIEMENTS

L'un de nous remercie le Centre National de la Recherche Scientifique qui lui a donné la possibilité d'entreprendre ces recherches. Il remercie également Mr. MAGNAN, Directeur du Laboratoire de Synthèse Atomique et d'Optique Protonique dans lequel il a eu toutes facilités pour commencer ce travail.

## RÉSUMÉ

Les isotopes radioactifs de mercure, platine, iridium, osmium et rhénium, produits par réactions de spallation dans l'or irradié avec des protons de 150 MeV, sont séparés sans entraîneurs par distillation dans un courant d'argon ou de chlore, et condensation dans un tube le long duquel est établi un gradient de température.

## SUMMARY

The radioactive isotopes of mercury, platinum, iridium, osmium and rhenium — products of bombardment processes in gold irradiated with protons at 150 MeV — are separated cleanly by distillation in a stream of argon or chlorine and by condensation in a tube possessing a temperature gradient.

## ZUSAMMENFASSUNG

Die radioaktiven Isotopen von Hg, Pt, Ir, Os und Re lassen sich durch Destillation in einem Strom von Argon oder Chlor sauber trennen, wenn die Kondensation in einer Röhre, die einen Temperaturabfall aufweist, erfolgt.

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# Short Communications

## Note sur la détection très sensible des gaz permanents en chromatographie gazeuse au moyen du detecteur à hélium métastable

L'idée déjà ancienne[1] du remplacement de l'argon par l'hélium pour l'analyse des gaz minéraux dont le potentiel d'ionisation est supérieur à 11.6 volts a été exploitée d'abord par BERRY[2] et tout récemment par WISEMAN[3], mais les auteurs ont toujours insisté sur la difficulté pratique d'une purification suffisante de l'hélium à moins de partir d'hélium atmosphérique très coûteux.

Nous avons obtenu récemment de très hautes sensibilités dans la détection de traces de gaz permanents au moyen d'un chromatographe Pye* standard, muni du détecteur classique de LOVELOCK[4] avec un procédé de purification extrêmement simple du gaz porteur.

Nous utilisons une colonne en verre de 1.20 m remplie de tamis moléculaires 13 A. L'hélium commercial à 99.9% traverse une colonne spirale de 8 m en acier inox de 6 mm de diamètre intérieur remplie de tamis moléculaires 5 A et plongeant dans l'azote liquide (Fig. 1). Il n'y a aucun joint en matière organique en aval de la spirale.

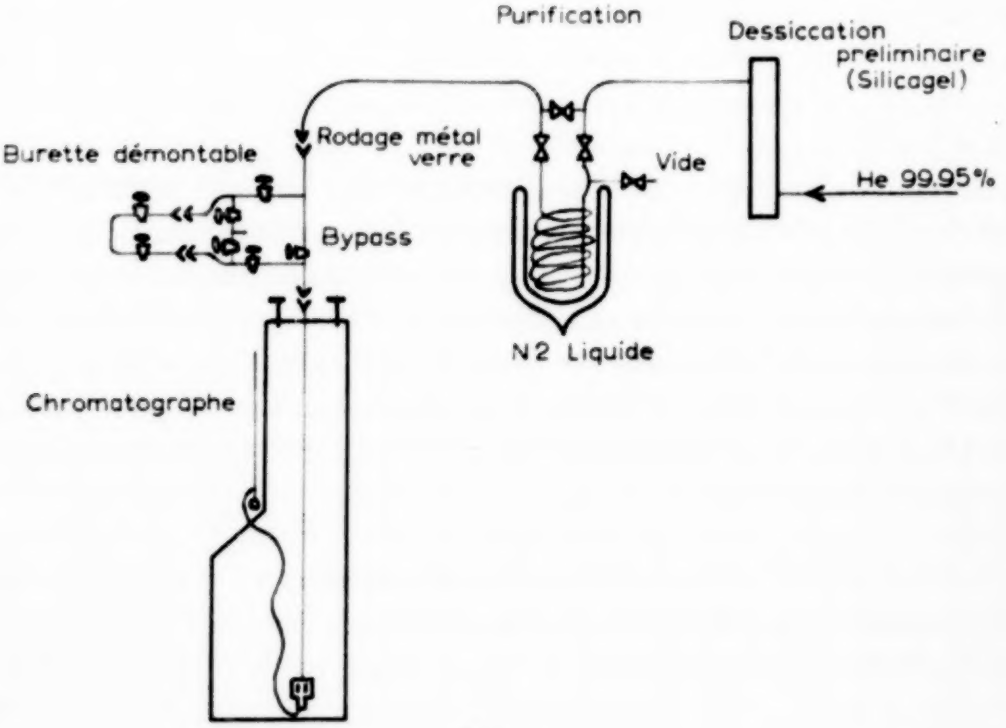

Fig. 1.

Les tamis 5 A sont régénérés sur place à 300° sous vide de pompe à palettes. Le chromatographe est étuvé 24 h à 200° sous hélium pur, après régénération extérieure énergique des tamis 13 A. La sensibilité de l'appareil s'améliore pendant 2 ou 3 jours. Au début nous avions déjà observé les pics négatifs et les pics en W que vient de signaler WISEMAN.

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* Avec une tension de 1000 volts.

Il est nécessaire d'avoir au moins 9 l/h d'hélium pour éviter la diffusion des gaz atmosphériques dans le détecteur, mais un débit plus élevé est inutile.

On peut facilement déceler des teneurs de 0.1 à 1 v.p.m. avec des éprouvettes de quelques $cm^3$. L'introduction de l'échantillon se traduit par un "à coup" positif. Fig. 2 représente un chromatogramme de traces de gaz permanents dans un composé fluoré, invisible du fait de son temps de rétention élevé.

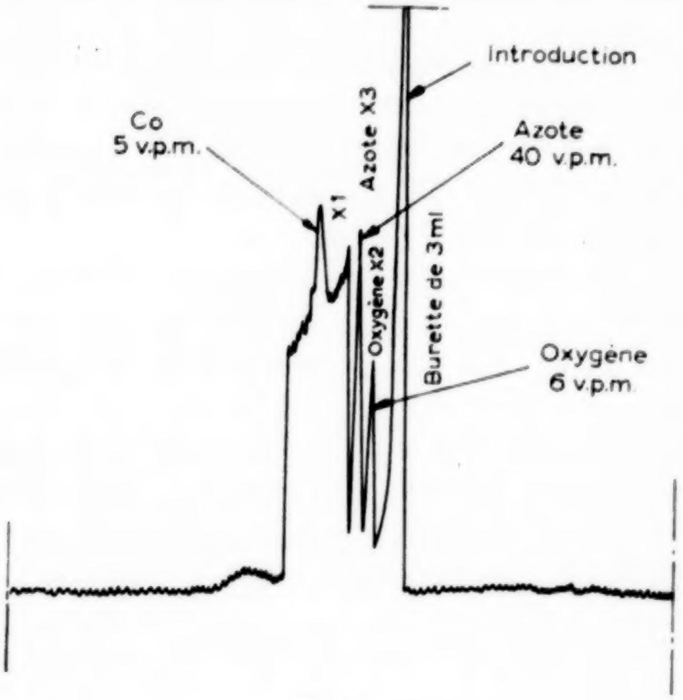

Fig. 2.

Cette méthode tire son intérêt de sa simplicité* et de son application possible à la recherche de traces d'oxyde de carbone ou d'oxygène dont l'importance industrielle est considérable. La chromatographie gazeuse fournit en particulier pour l'analyse de traces d'oxygène moléculaire une méthode de détection beaucoup plus spécifique que la plupart des méthodes actuelles faisant intervenir des réactions d'oxydation. Ce travail a été effectué dans le cadre d'un contrat avec le Commissariat Français à l'Énergie Atomique. Nous remercions sincèrement la Direction de ce Service d'avoir autorisé cette publication.

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Reçu le 25 juillet, 1961

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* L'emploi plusieurs fois signalé du même appareil comme détecteur à mobilité d'électrons avec de l'hélium plus ou moins volontairement contaminé[5], est d'un emploi moins commode et conduit à une moindre sensibilité.

# The reactions of diphenylcarbazide and diphenylcarbazone with cations

In the course of research on the stability constants of diphenylcarbazide and diphenylcarbazone complexes with B-group cations, with the object of completing the "dithizone system"[1], several interesting observations were made. These are summarized in the following paragraphs.

## *Reagents*

Diphenylcarbazone, on titration with base, proves to be a monobasic acid; spectrophotometric determination of the partition equilibrium in the system carbon tetrachloride–water as controlled by the pH, gives for $K_{diss.}$ the value $(2.2 \pm 0.2) \cdot 10^{-8}$, whereas diphenylcarbazide is a neutral compound. The visible spectrum of diphenylcarbazone in toluene solution shows a strong maximum at 467 mμ, and a weaker one at 565 mμ. Irradiation of the solution with UV-light makes the latter maximum increase, while the former decreases.

## *Complex formation*

There is no agreement in the literature whether only diphenylcarbazone[2] or both the carbazide and carbazone[3,4] form metal complexes. We have shown that with some non-oxidizing cations (zinc, nickel(II), lead(II) and cadmium) colored complexes are found only with diphenylcarbazone; the carbazide does not react with them if it is freshly recrystallized from alcohol. On the other hand, oxidizing cations (mercury(I) and (II), copper(II) and iron(III)) do react with diphenylcarbazide. Subsequent acid decomposition of the extracted or precipitated compounds showed, however, that the carbazone and not the carbazide is bound. The acid solution does not react with chromic acid, which is a reagent for diphenylcarbazone[5]. Thus complex formation actually occurs with diphenylcarbazone which is first formed from the carbazide by an oxidation reaction with the cations of mercury etc. So far, we have been unable to find any diphenylcarbazide compounds alongside the carbazone complexes.

The diphenylcarbazone complexes investigated are more easily oxidized by atmospheric oxygen than is diphenylcarbazone itself.

We have established that the diphenylcarbazone complexes of mercury(I) and (II) and copper(II) are stable in the solid state; in toluene solution they decompose to form the oxidation product of diphenylcarbazone, *i.e.* diphenylcarbodiazone, which can be identified by means of the absorption spectrum. The other decomposition products are mercury and probably copper(I). Irradiation with UV-light accelerates such decomposition. The other investigated complexes do not show such decomposition in toluene solution.

From the Tyndall effect we concluded that diphenylcarbazone and the mercury(I) and (II) and cadmium(II) complexes are colloids in an alcohol–water solution.

Job curves and extinction measurements on solutions of the lowest metal-diphenylcarbazone complexes with varying excesses of the carbazone, prove that both mercury(I) and (II) and nickel(II) form 1 : 1 and 1 : 2 compounds (M:diphenylcarbazone), comparable to the primary and secondary dithizonates; lead(II) and zinc(II) give only 1 : 2 compounds.

The dissociation constants of the complexes, measured spectrophotometrically by using the extraction method, are several orders greater than the constants of the corresponding dithizonates. For instance:

$$\frac{(\mathrm{Hg}^{++})_w\ (\mathrm{dco})^2_t}{(1:2\ \mathrm{compl.})_t\ (\mathrm{H}^+)^2_w} = 5.2\cdot 10^{-6}$$

where w = water, t = toluene, and dco = diphenylcarbazone, whereas the corresponding constant for dithizone[1] in the system carbon tetrachloride–water is $1.4\cdot 10^{-27}$.

Mercury(I) and (II) nitrate and perchlorate solutions show a strong ageing effect: the reaction of freshly prepared solutions with diphenylcarbazone decreases by 40–80% in 20 h, depending on the pH; the only possible explanation proved to be slow hydrolysis. This behaviour may be compared with that of rhodium(III) solutions[6].

For the complexes studied no linear relationship exists between $K$ and $\lambda_{\mathrm{max.}}$ in the visible spectrum[7].

Infrared spectra of the solid (1 : 1) complexes of mercury(I) and (II) and cadmium(II) (in KBr discs) do not show any absorption at 5.85 $\mu$, the wavelength of the C=O bond in diphenylcarbazone. This is an indication of M-O bonding in these complexes, with the carbazone in the enolic form.

Studies on the properties and dissociation constants of the diphenylcarbazone compounds are being continued; more detailed publication will follow in due course.

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Received July 23rd, 1961

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## ERRATUM

*Anal. Chim. Acta*, 24 (1961) 410, the first paragraph of INTRODUCTION, line 6 should read:

. . . . . for convenience, a $\gamma$-ray emitted from a nuclide formed . . . . .

# SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

## Vol. 25, No. 6, December 1961

### GRAPHICAL ANALYSIS OF PHOTOMETRIC INDICATOR TITRATION DATA

Three equations have been presented for the linear extrapolation of photometric indicator titration data to yield the end-point and the equilibrium constant for the titration reaction $BHA + I \rightleftarrows IHA + B$, which controls the color change of the indicator I in the titration of the base B with the acid HA.

K. A. Connors and T. Higuchi, *Anal. Chim. Acta*, 25 (1961) 509–512

### DIRECT TITRATION OF ALUMINIUM, AND STEPWISE TITRATION OF IRON(III) AND ALUMINIUM WITH EDTA AND 3-HYDROXY-2-NAPHTHOIC ACID AS INDICATOR

Aluminium can be titrated directly at pH 3 with 0.05 *M* EDTA in presence of 3-hydroxy-2-naphthoic acid as a fluorescent indicator. Iron(III) can be titrated with the use of the same indicator in the presence of aluminium. A step-wise titration of iron at pH 2 and aluminium at pH 3 is possible.

H. Kristiansen, *Anal. Chim. Acta*, 25 (1961) 513–515

### AUTOMATIC TITRATION OF IRON IN BLOOD

A method is described for the determination of iron in blood which combines a rapid digestion procedure and automatic titration. The method is more rapid than conventional methods and as accurate. After wet ashing of the blood, an excess of standard EDTA is added, and back-titrated automatically with copper solution and Calcein W as indicator. The total time for a determination is about 15 min.

T. P. Hadjiioannou and C. Vassiliades, *Anal. Chim. Acta*, 25 (1961) 516–519

### DETERMINATION OF TRACES OF BISMUTH WITH DITHIZONE AFTER IODIDE EXTRACTION

A method for the determination of µg quantities of bismuth in the presence of much iron, calcium, magnesium and phosphate is described. Bismuth is extracted as $BiI_3$ by isoamyl acetate from perchloric acid medium in the presence of ascorbic acid and sulfite, and determined as dithizonate in the isoamyl acetate phase. The method is intended particularly for natural materials such as silicates and phosphates in which bismuth exceeds a few tenths of a p.p.m. and lead is present in amounts below 500 p.p.m.

H. A. Mottola and E. B. Sandell, *Anal. Chim. Acta*, 25 (1961) 520–524

## LIQUID–LIQUID EXTRACTION OF IRON(III) WITH 2-THENOYLTRIFLUOROACETONE FROM A NITRATE SYSTEM, AND DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

Iron extraction with TTA from concentrated nitric acid and ammonium nitrate solutions is considered with regard to reagent concentrations and the time and temperature of extraction. It is possible to determine 0.2 to 10 $\mu$g/ml of iron directly in the organic phase by measuring its absorbance at 510 m$\mu$. Large amounts of several metallic ions can be present, *e.g.* iron can be determined in U, Co, Al, Ni.

C. TESTA, *Anal. Chim. Acta*, 25 (1961) 525–532

## TITRIMETRIC DETERMINATION OF THALLIUM(I) WITH LEAD(IV) ACETATE

*(in German)*

Thallium(I) can be determined by direct potentiometric titration with lead tetraacetate solution in hydrochloric acid media. As little as 10 $\mu$g of thallium in 35 ml of solution can be determined accurately.

A. BERKA, J. DOLEŽAL, I. NĚMEC AND J. ZÝKA, *Anal. Chim. Acta*, 25 (1961) 533–537

## DETERMINATION OF AMINES, PYRIDINE AND NICOTINE BY THERMOMETRIC TITRATION

Thermometric titrations with acids and sodium nitrite solution are described for the determination of methylamine, ethylenediamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine. The method is applicable to dilute aqueous solutions; alcohols and phenol do not interfere. Mixtures of aniline, pyridine and diethylamine or ethylenediamine can be analysed. The accuracy of the method is ±1.5%.

R. D. DAFTARY AND B. C. HALDAR, *Anal. Chim. Acta*, 25 (1961) 538–541

## A NEW METHOD FOR DETERMINATION OF TRACES OF CARBON

### APPLICATION TO SILICON AND GERMANIUM

*(in French)*

A new method is proposed for the determination of traces of carbon in silicon and germanium. The sample is converted to the sulphide by treatment with sulphur vapour in a sealed tube at 1000–1100°. Carbon thus forms carbon disulphide which is determined colorimetrically as diethyldithiocarbamate after dissolution in an organic solvent and addition of diethylamine. Results show that silicon "for semi-conductors" contains 500–2000 p.p.m. of carbon. However, germanium contains only a few p.p.m. of carbon.

L. DUCRET AND CL. CORNET, *Anal. Chim. Acta*, 25 (1961) 542–545

## ANALYTICAL APPLICATION OF DISTILLATION OF CARBON DIOXIDE

### I. DETERMINATION OF FORMIC ACID (FORMATE) BY OXIDATION WITH MERCURY(II) CHLORIDE

*(in German)*

Formic acid and formates are best determined by selective oxidation with mercury(II) chloride. The gravimetric determination of the mercury(I) chloride formed is tedious, and the authors propose a simple distillation method for determination of the carbon dioxide formed. Rapid titrimetric determination with 0.1 or 0.01 *N* solutions is possible.

L. Maros, M. Pintér-Szakács and E. Schulek, *Anal. Chim. Acta*, 25 (1961) 546–550

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## CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF VARIOUS ELEMENTS WITH $\alpha$-NITROSO-$\beta$-NAPHTHOL

### DETERMINATION OF URANIUM IN SEAWATER

The co-crystallization of ultramicro quantities of various elements with $\alpha$-nitroso-$\beta$-naphthol was investigated. Radiotracer techniques were employed to measure the quantitative removal of these elements from aqueous solutions. Conditions were developed for the separation of cerium(III), zinc, iron(III), cobalt(II), zirconium and uranium(VI) by this process. Plutonium(IV) and ruthenium(III) co-crystallized less completely while sodium, strontium and antimony(III) remained largely associated with the mother liquor. The process was applied in the determination of uranium in seawater. The measured amount was 3.1 ± 0.1 $\mu$g uranium/l.

H. V. Weiss, M. G. Lai and A. Gillespie, *Anal. Chim. Acta*, 25 (1961) 550–556

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## THE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM IN PLANT EXTRACTS WITH SPECIAL REFERENCE TO INTERFERENCE EFFECTS

The flame photometric determination of sodium and potassium in plant ash extracts has been studied with particular reference to interferences; the instrument used was a Beckman spectrophotometer model DU, with a flame attachment of the total consumption burner type. The ions Na, K, Ca, Mg, $NO_3^-$, $PO_4^{-3}$ and $SO_4^{-2}$ were tested; sodium and potassium had a strong mutual enhancement effect which could cause errors up to 25%, but which could be compensated by adding the interfering elements to the standards. Interference effects prevented the direct determination of calcium in plant ash extracts, hence calcium oxalate was precipitated and dissolved and the solution was read in the flame photometer. This method was preferable to chemical methods particularly when sodium and potassium were to be determined in the same sample.

G. N. Havre, *Anal. Chim. Acta*, 25 (1961) 557–566

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## A BASIS FOR THE DETERMINATION OF DISSOLVED OXYGEN BY ELECTRON SPIN RESONANCE SPECTROSCOPY

The ESR spectrum of certain free radicals in solutions is strongly affected by dissolved oxygen. This phenomena can be used as a basis of a simple method for the determination of molecular oxygen in organic solutions. It should be of particular value in the quantitative determination of low concentrations of oxygen, *i.e.*, in the region of $10^{-5}$ to $10^{-3}$ normal.

R. B. Ingalls and G. A. Pearson, *Anal. Chim. Acta*, 25 (1961) 566–569

## RADIOMETRIC TRACE ANALYSIS

### QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH PHOSPHATE-$^{32}$P

A method is described for the selective determination of lead in paper chromatograms, down to 1 μg (standard deviation 11%). After development and drying, the lead spot is sprayed with a $Na_2H^{32}PO_4$ solution and dried. Excess reagent and alkaline earth phosphates are eluted with a borax–oxalate buffer of pH 8.0. Eventually, the radio-activity of the lead spot is measured. The filter paper renders the method about 40 times more sensitive than existing radiometric techniques with phosphate-$^{32}$P. The method can be modified for the simultaneous determination of many cations.

P. C. van Erkelens, *Anal. Chim. Acta*, 25 (1961) 570–578

## PREPARATION OF STOICHIOMETRIC $U_3O_8$

The preparation of stoichiometric $U_3O_8$ depends on the starting uranium compound, sample size, temperature, duration of ignition, and chemical alteration of the starting compound. Stoichiometric $U_3O_8$ was prepared in 10-g quantities from uranyl fluoride and uranium peroxide by ignition at 850° for 16 h, and from uranyl nitrate and uranium trioxide by ignition at 1000° for 16 h followed by re-ignition at 850° to constant weight. The ignition time required to produce a stoichiometric $U_3O_8$ may be decreased for many compounds by (*1*) converting the starting compound to uranium peroxide, or (*2*) treating the sample with hydrofluoric acid before ignition at 850° for 16 h.

G. S. Petit and C. A. Kienberger, *Anal. Chim. Acta*, 25 (1961) 579–586

## THE DETERMINATION OF URANIUM IN FAIRLY PURE BERYLLIUM METAL BY NEUTRON ACTIVATION AND GAMMA SPECTROMETRY

A method is described for the determination of trace quantities of uranium in beryllium metal. The beryllium samples are irradiated in "polytainers" for 1½ to 2 h in a flux of $10^{12}$ neutrons/cm$^2$/sec (as in BEPO), allowed to stand for 24 h, then measured directly without any further treatment on a $\gamma$-spectrometer. The radio-nuclide used is 2.33-day $^{239}$Np, which produces a satisfactory photo-peak with a 1″ × 1½″ NaI(Tl) crystal and single-channel $\gamma$-spectrometer. Dilute solutions (50 μg/ml) of uranium are used as standards, and after irradiation, prepared in similar polytainers as used for the samples. As little as 1 p.p.m. of uranium can be determined in 0.5-g samples of beryllium metal; for greater sensitivity radio-chemical separations would be required. Much of the radioactivity produced in the sample is due to the impurities it contains, and it is this radioactivity which limits the sensitivity of the direct $\gamma$-spectrometric method. Full details of the method are given, and various factors which may be a source of error are discussed.

A. A. Smales, D. Mapper and A. P. Seyfang, *Anal. Chim. Acta*, 25 (1961) 587–597

## A SOLVENT EXTRACTION SYSTEM FOR 2,4-DINITROPHENYLHYDRAZONES

### APPLICATION TO THE HYDRAZONES OF OXIDATION PRODUCTS OF β-ALANINE AND HYDROLYZED CALCIUM *d*-PANTOTHENATE

*(Short Communication)*

T. Panalaks, *Anal. Chim. Acta*, 25 (1961) 598–599

# GRAPHICAL ANALYSIS OF PHOTOMETRIC INDICATOR TITRATION DATA

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(Received March 27th, 1961)

The introduction of linear extrapolation procedures for the treatment of spectrophotometric indicator titration data has greatly increased the applicability of photometric titration methods[1,2]. The most fruitful use of these techniques has employed the so-called Type II system[1,3,4], in which the indicator color change is controlled essentially by the equilibrium

$$\mathrm{BHA} + \mathrm{I} \rightleftarrows \mathrm{IHA} + \mathrm{B} \tag{1}$$

where the sample base B and the indicator base I compete for the titrant acid HA. (The color change will also be affected, to a greater or lesser extent, by solvolysis of the salt formed in the titration[3,4]). The titration of a sample acid with a base is completely analogous. The titration equation which has been applied to this system is

$$\frac{1}{X} = \frac{K_{ex}}{S}\frac{\mathrm{I}_b}{\mathrm{I}_a} + \frac{1}{S} \tag{2}$$

where $X$ is the volume of standard titrant acid solution added, $S$ is the volume of titrant equivalent to the base initially present, $K_{ex}$ is the equilibrium constant (referred to as the exchange constant) for reaction (1), and $\mathrm{I}_b/\mathrm{I}_a$ is the spectrophotometrically measured ratio of indicator in the base form to that in the acid form. A plot of $\mathrm{I}_b/\mathrm{I}_a$ *vs.* $1/X$ yields a straight line, the intercept on the $1/X$ axis being equal to $1/S$. From the slope, $K_{ex}$ can be calculated by combination with the value for $S$ found from the intercept[1]. Alternatively the exchange constant can be determined from the intercept on the $\mathrm{I}_b/\mathrm{I}_a$ axis, which is equal to $-1/K_{ex}$.

The titration equation can be rearranged into other forms which in some cases might permit more suitable treatment of the data. Eqn. (3) is obtained by rearrangement of eqn. (2). A plot

$$X(\mathrm{I}_b/\mathrm{I}_a) = S/K_{ex} - X/K_{ex} \tag{3}$$

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of the quantity $X(I_b/I_a)$ *vs.* $X$ should give a line of slope $-1/K_{ex}$; the intercept on the $X$ axis is equal to $S$, while that on the $X(I_b/I_a)$ axis is $S/K_{ex}$. Eqn. (4) gives another equivalent form

$$I_a/I_b = (I_a/I_b)\frac{S}{X} - K_{ex} \tag{4}$$

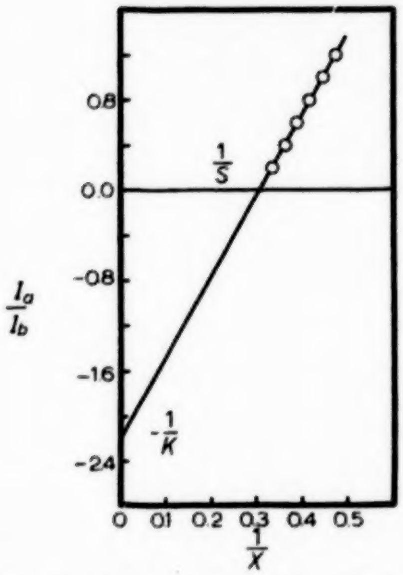

Fig. 1. Plot according to eqn. (2) for the photometric titration of 19.36 mg of urea with 0.0980 $N$ perchloric acid in acetic acid solution; Nile Blue A indicator. The quantities determined from the intercepts are indicated. Slope = $S/K$.

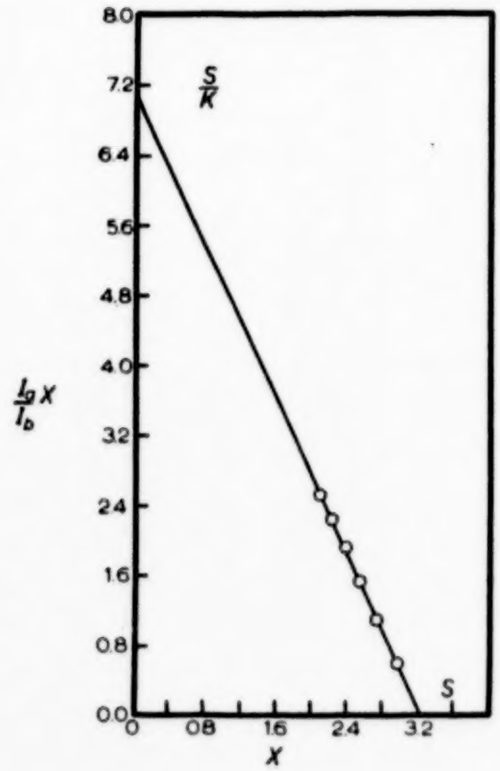

Fig. 2. Plot according to eqn. (3) of the titration of urea; see legend, Fig. 1, for details. Slope = $-1/K$.

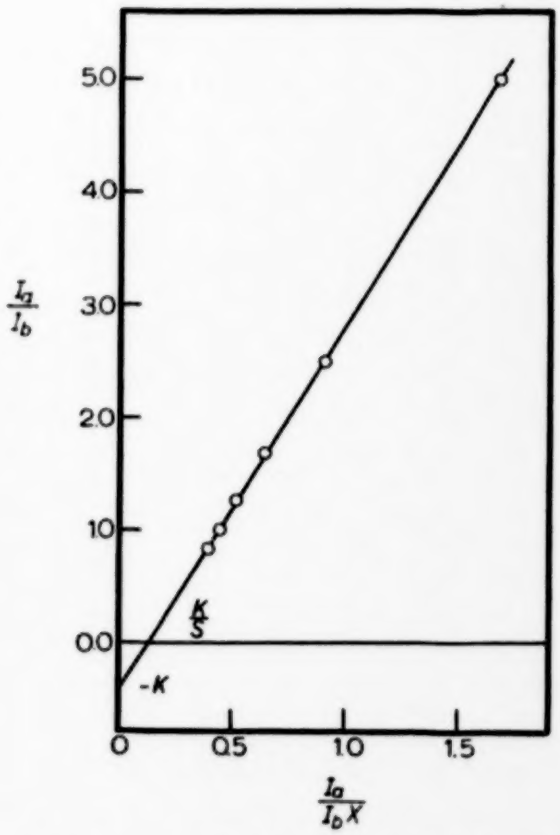

Fig. 3. Plot according to eqn. (4) of the titration of urea; see legend, Fig. 1, for details. Slope = $S$.

of the relation; a plot of $I_a/I_b$ *vs.* $(I_a/I_b)(1/X)$ is linear with a slope equal to $S$. The intercept on the $I_a/I_b$ axis is $-K_{ex}$ and on the other axis it is $K_{ex}/S$.

In Figs. 1, 2, and 3 are given plots according to eqns. (2), (3), and (4), respectively, for the photometric titration of urea with perchloric acid in acetic acid solution, Nile Blue A being the indicator. (The data have been corrected for the effect of solvolysis, as described earlier[3]). The values of $S$ and $K_{ex}$ determined by the three plots are in good agreement.

The method of choice for the treatment of Type II titration data will depend upon the particular system and upon the information desired. An intercept will be located most accurately when the angle between the line and the axis most nearly approaches 90°. This condition can be realized for the plot according to eqn. (2) by increasing the value of $S$ (that is, by using a larger sample) or by decreasing the value of $K_{ex}$ (which can be done by changing the indicator), thus permitting accurate determination of $S$, but resulting in decreased accuracy in the value for $K_{ex}$. In contrast to this method, the slope of the plot according to eqn. (3) is independent of sample size. An advantage of this second method is that the end-point, $S$, is obtained directly, without further calculation, from an intercept. In the third plot (eqn. (4)) the extrapolation may be made principally with points obtained early in the titration, and this may be advantageous particularly if the titration cannot be brought nearly to completion, for example because of insolubility of the salt formed. The prime difference from the practical standpoint between eqns. (2) and (3) and eqn. (4) is that the end-point is calculated from an intercept in the first two cases and from the slope in the last case. For this reason eqn. (4) will permit more accurate graphical determination of the end-point in some instances.

In those cases in which extensive solvolysis during the titration results in deviations from the simple eqns. (2), (3), and (4), it is necessary to apply a correction. This modification, which is essentially a difference titration, was developed on the basis of eqn. (2)[3]. However, it may be carried out with the other equations also, and the calculations are in fact simplified when eqn. (3) is employed for this purpose. Plots of $I_b/I_a$ *vs.* $X$ are made for the two titrations (which differ only in sample size). The quantity $(X_2 - X_1)$ is then read from this graph at rounded values of $I_b/I_a$, and finally the plot of $(X_2 - X_1)(I_b/I_a)$ *vs.* $(X_2 - X_1)$ is made, as in Fig. 2.

An equation relating the apparent indicator salt formation constant in acetic acid to the water concentration in the acetic acid[5] may also be put into three linear forms analogous to eqns. (2), (3), and (4). In fact, any equation of the form

$$x = \frac{y}{a + by} \tag{5}$$

where $a$ and $b$ are constants (this is the equation of an equilateral hyperbola), can be written in the linear forms

$$1/x = a/y + b \tag{6}$$

$$x/y = -bx/a + 1/a \tag{7}$$

$$y/x = by + a \tag{8}$$

which correspond to eqns. (2), (3), and (4) above. Other physically useful relations with the form of eqn. (5) are the Michaelis-Menten equation describing the kinetics of enzyme catalyzed reactions[6], the Langmuir adsorption equation[7], and empirical modifications of Einstein's equation for the viscosity of suspensions[8].

## SUMMARY

Three equations have been presented for the linear extrapolation of photometric indicator titration data to yield the end-point and the equilibrium constant for the titration reaction $BHA + I \rightleftarrows IHA + B$, which controls the color change of the indicator I in the titration of the base B with the acid HA.

## RÉSUMÉ

Les auteurs ont effectué une étude sur les procédés d'extrapolation linéaire lors de titrages photométriques, pour la détermination du point final et de la constante d'équilibre.

## ZUSAMMENFASSUNG

Es werden 3 Gleichungen gegeben für die lineare Extrapolation der Daten einer photometrischen Titration zur Bestimmung des Endpunktes sowie der Gleichgewichtskonstante, welche den Farbumschlag des Indikators bei der Basen–Säure Titration bestimmt.

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# DIRECT TITRATION OF ALUMINIUM, AND STEPWISE TITRATION OF IRON(III) AND ALUMINIUM WITH EDTA AND 3-HYDROXY-2-NAPHTHOIC ACID AS INDICATOR

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(Received March 29th, 1961)

According to CHERKESOV[1], 3-hydroxy-2-naphthoic acid gives a specific and highly sensitive fluorescent test for aluminium. A solution of the sodium salt of 3-hydroxy-2-naphthoic acid in water gives a green fluorescence at pH 3 under ultraviolet light. With aluminium the fluorescence is blue at the same pH value. Owing to this change in fluorescence, the sodium salt of 3-hydroxy-2-naphthoic acid is applicable as a metal indicator in the direct EDTA titration of aluminium.

PANDE AND SRIVASTAVA[2] introduced 3-hydroxy-2-naphthoic acid as an indicator for the EDTA titration of iron(III), but they found that aluminium interfered in this titration. In this paper a method is presented in which aluminium does not interfere. In a mixture of iron(III) and aluminium, the iron is first determined by titration with EDTA, 3-hydroxy-2-naphthoic acid being used as indicator. By further titration in ultraviolet light with the same indicator, the aluminium is determined directly.

## EXPERIMENTAL

### *Indicator solution*

3-Hydroxy-2-naphthoic acid was recrystallised from hot water, and a 0.1% solution of the sodium salt in distilled water was prepared.

### *Standard solutions*

A 0.05 *M* EDTA standard solution was prepared from the disodium salt of ethylenediaminetetraacetic acid standardized in the usual way.

The aluminium standard solution was prepared by dissolving 1.0000 g of aluminium (super pure; 99.997% Al) in 1:1 hydrochloric acid and diluting to 1 l.

The iron(III) standard solution was prepared by dissolving 1.9031 g of high purity iron (spectrographically standardized) in hydrochloric acid, oxidizing with nitric acid and diluting to 1 l.

All other chemicals used were of reagent grade quality. For the pH determinations, a Beckman pH-meter model H-2 was employed.

### *Titration of aluminium*

The aluminium solution to be titrated was diluted to about 100 ml and 1 ml of the indicator solution was added. The pH value of the sample solution was adjusted to about 3 by adding glycine. The rate of reaction between aluminium and EDTA is increased by increasing the temperature[3], but the equilibrium

$$Al^{+3} + 3\,H_2O \rightleftarrows Al(OH)_3 + 3\,H^+$$

is displaced to the right at higher temperatures and because of the formation of colloidal aluminium hydroxide, the end-point is reached long before the equivalence point. The best temperature for this titration, however, was found to be about 50°, the titration being done slowly near the end-point.

The observations were made in ultraviolet light. The end-point was reached when the fluorescence changes from blue to green. The results of a series of titrations of aluminium are given in Table I.

TABLE I

TITRATION OF ALUMINIUM WITH 0.04950 *M* EDTA SOLUTION AND 3-HYDROXY-2-NAPHTHOIC ACID

Buffer: glycine–HCl; pH 3; volume of solution before titration: about 100 ml

| *Al taken* *mg* | *EDTA used* *ml* | *Al found* *mg* | *Relative error* *%* |
|---|---|---|---|
| 25 | 18.71 | 24.99 | −0.05 |
| 25 | 18.68 | 24.95 | −0.2 |
| 25 | 18.68 | 24.95 | −0.2 |
| 25 | 18.70 | 24.97 | −0.1 |
| 25 | 18.71 | 24.99 | −0.05 |
| 25 | 18.69 | 24.96 | −0.2 |
| 25 | 18.70 | 24.97 | −0.1 |
| 25 | 18.71 | 24.99 | −0.05 |

TABLE II

TITRATION OF IRON(III) WITH 0.04950 *M* EDTA SOLUTION IN PRESENCE OF 3-HYDROXY-2-NAPHTHOIC ACID INDICATOR AND VARIOUS AMOUNTS OF ALUMINIUM

Buffer: glycine–HCl; pH 2; volume of solution before titration: about 100 ml

| *Fe taken* *mg* | *Al present* *mg* | *EDTA used* *ml* | *Fe found* *mg* | *Relative error* *%* |
|---|---|---|---|---|
| 9.515 | 0 | 3.43 | 9.48 | −0.4 |
| 9.515 | 60 | 3.45 | 9.54 | +0.2 |
| 9.515 | 60 | 3.44 | 9.51 | ±0.0 |
| 47.578 | 60 | 17.20 | 47.55 | −0.05 |
| 47.578 | 60 | 17.19 | 47.52 | −0.1 |
| 47.578 | 100 | 17.21 | 47.58 | ±0.0 |
| 47.578 | 100 | 17.22 | 47.61 | +0.1 |
| 47.578 | 500 | 17.20 | 47.55 | −0.05 |
| 47.578 | 500 | 17.24 | 47.66 | +0.2 |

### *Titration of iron(III) in the presence of aluminium*

As mentioned above, the chelate formation between aluminium and EDTA is influenced by the temperature. If the procedure given by Pande and Srivastava[2] is used aluminium interferes in the determination of iron. However, when this titration was carried out in ice-cooled solution aluminium did not interfere. The titrations were carried out with a piece of ice in the titration flask. The end-point was reached when the colour changed from blue to yellow.

In Table II the results of a series of titrations of known amounts of iron(III) in the presence of various amounts of aluminium are recorded.

### *Stepwise titration of iron(III) and aluminium*

The difference in the effective stability constants of iron(III) and aluminium with EDTA at pH 2, together with the slow reaction rate of aluminium with EDTA at low temperatures, permitted the titration of iron in the presence of aluminium. After the end-point of the titration of iron had been reached, the sample solution was heated to about 50° and the pH adjusted to about 3 by adding 10 ml of a 10% solution of glycine.

The titration was then continued in ultraviolet light in a dark room and the end-point was reached when the fluorescence changed from blue to green. The yellow colour of the sample solution weakened the blue fluorescence of the aluminium–3-hydroxy-2-naphthoic acid complex, but the end-point was accurately determined by comparison with a solution of the indicator.

In Table III the result of a series of titrations of known amounts of iron(III) and aluminium are recorded.

TABLE III

TITRATION OF IRON(III) AND ALUMINIUM WITH 0.04950 *M* EDTA SOLUTION AND 3-HYDROXY-2-NAPHTHOIC ACID INDICATOR

Buffer: glycine–HCl; volume of the solution before titration: about 200 ml

| *Fe taken* *mg* | *Al taken* *mg* | *Fe found* *mg* | *Relative error* % | *Al found* *mg* | *Relative error* % |
|---|---|---|---|---|---|
| 12.40 | 30.00 | 12.41 | +0.1 | 29.86 | —0.1 |
| 12.40 | 30.00 | 12.36 | —0.3 | 29.97 | —0.1 |
| 24.81 | 25.00 | 24.74 | —0.3 | 25.08 | +0.4 |
| 24.81 | 25.00 | 24.77 | —0.1 | 24.97 | —0.1 |
| 24.81 | 25.00 | 24.80 | ±0.0 | 25.02 | +0.1 |
| 49.62 | 25.00 | 49.59 | —0.1 | 25.00 | ±0.0 |
| 62.02 | 25.00 | 61.87 | —0.2 | 24.87 | —0.5 |
| 62.02 | 25.00 | 61.81 | —0.3 | 24.95 | —0.2 |

## SUMMARY

Aluminium can be titrated directly at pH 3 with 0.05 *M* EDTA in presence of 3-hydroxy-2-naphthoic acid as a fluorescent indicator. Iron(III) can be titrated with the use of the same indicator in the presence of aluminium. A step-wise titration of iron at pH 2 and aluminium at pH 3 is possible.

## RÉSUMÉ

Une méthode est décrite pour le titrage de l'aluminium, au moyen d'EDTA, en présence d'acide hydroxy-3-naphtoïque-2 comme indicateur de fluorescence. Ce procédé permet également de doser le fer et l'aluminium, l'un en présence de l'autre.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur direkten Titration von Aluminium mit EDTA und 3-Hydroxy-2-naphtoesäure als Fluoreszenzindikator. Durch Einhaltung bestimmter pH Werte kann auch Eisen(III) neben Aluminium durch stufenweise Titration bestimmt werden.

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# AUTOMATIC TITRATION OF IRON IN BLOOD

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(Received March 30th, 1961)

## INTRODUCTION

A number of techniques and procedures have been used for the analysis of iron in blood. After wet or dry ashing of the blood, the iron is determined in the ash solution by titrimetric or colorimetric methods. Chelometric titrations using disodium ethylenediaminetetraacetate (EDTA) as titrant and metal indicators have been proposed for the more rapid analysis of iron in blood. HABERLI[1] used Tiron as the indicator and titrated the mixture at a temperature of 50°. BONATI AND CHIARONI[2] used sulfosalicylic acid indicator for the direct EDTA titration of iron.

For the wet decomposition of organic matter various acids and oxidizing agents have been used. In the proposed procedure a more rapid method of oxidizing the organic matter with a combination of sulfuric acid, hydrogen peroxide, and nitric acid is used. After wet ashing an excess of standard EDTA solution is added to the sample; the excess of EDTA is then back-titrated automatically with standard copper solution using Calcein W as indicator. The second derivative technique is used for the automatic termination at the end-point[3].

The titration is completed rapidly, requiring only about 30 sec. The total time required for sample manipulation — wet ashing, pH adjustment, etc. — is about 15 min. The automatic end-point is reproducible and accurate to within 0.02 ml of 0.01 *M* EDTA solution, and the results check closely with those obtained using *o*-phenanthroline[4].

## APPARATUS

The Sargent-Malmstadt "Spectro-Electro" titrator was used[5].

A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill stopcocks and titrant reservoir was used for the standard copper solution.

## REAGENTS

*Standard $10^{-2}$ M copper solution.* Dissolve 0.6354 g reagent grade copper sheet in a slight excess of concentrated nitric acid and dilute to the mark in a 1-l volumetric flask with deionized water.

*EDTA solution.* Dry the disodium salt of ethylenediaminetetraacetic acid (EDTA) at 80° for 2 h. Dissolve 3.73 g of the dried salt in deionized water and dilute to 1 l.

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Standardize this solution against the standard copper solution and store it in a polyethylene bottle.

*Buffer solution*. Mix 638 ml of 1 *N* acetic acid with 362 ml of 1 *M* sodium acetate, reagent grade.

*Sodium hydroxide*: 10% (iron-free) aqueous solution.

*Calcein W indicator*: 0.2% in 0.001 *N* sodium hydroxide.

## PROCEDURE

### *Preparation of automatic titrator*

Prepare the "Spectro-Electro" titrator as previously reported[3], but set the titrant delivery rate at about 5 ml/min.

### *Standardization of EDTA solution*

Pipet a 4-ml aliquot of EDTA solution into a 100-ml tall-form beaker, add 55 ml of deionized water, 4 ml of the buffer solution, and 4 drops of the indicator solution. Insert the beaker in the titrator, push the start button to start the delivery of titrant and read the buret after automatic termination at the end-point.

### *Preparation of blood samples*

Pipet 1.00 ml of blood to the bottom of a 150-ml Kjeldahl digestion flask. Wash the pipet by sucking a few drops of water up and down the pipet from a small tube and then transfer the washings by the pipet to the flask. Add 1 ml of concentrated sulfuric acid, mix by swirling, and add 5 ml of perhydrol. Heat the mixture, gently at first over a low flame to avoid excessive foaming, and then boil vigorously until the digestion mixture turns brown and white fumes of sulfur trioxide are evolved (about 8 min). Discontinue the heating for a few sec, add dropwise 0.2 ml of concentrated nitric acid, and heat again vigorously until the solution becomes straw yellow and white fumes are evolved. Remove the flask and let it cool. Dilute the contents of the flask with 12 ml of distilled water, transfer it into a 100-ml tall-form beaker, and rinse the flask twice with 10-ml aliquots of distilled water. Pipet 3 ml of EDTA solution into the beaker, and add enough 10% sodium hydroxide solution (about 12–14 ml) under vigorous stirring with a magnetic stirrer to bring the pH to 2.5 (use a pH-meter). Add 15 ml of the buffer solution and 4 drops of the indicator solution. Insert the beaker in the titrator, start the stirrer, push the start button after a few seconds, and titrate as in the standardization procedure.

## CALCULATIONS

When 1 ml of blood is taken for titration, iron can be calculated as follows:

$$A \cdot (3 - B - 0.07) \cdot 100 = \text{mg Fe/100 ml of blood} \qquad (1)$$

where $A$ = mg Fe/ml of EDTA solution [$A = 2.24/(C - 0.07)$, where $C$ = ml of copper solution used in the standardization of EDTA solution] and $B$ = ml of copper solution used for the back-titration of excess EDTA.

## RESULTS AND DISCUSSION

Blood samples of different origin — human, calf, lamb, pork — were analyzed by the proposed method and the results obtained compared favorably with those obtained with *o*-phenanthroline (Table I).

To check the reproducibility of the proposed complete procedure for blood-iron analysis, a series of determinations was carried out for 8 identical samples of blood. The results are tabulated in Table II. The standard deviation is 0.7 mg Fe/100 ml of blood.

TABLE I

COMPARISON OF AUTOMATIC TITRATION AND *o*-PHENANTHROLINE RESULTS FOR THE DETERMINATION OF IRON IN BLOOD

| *Sample No.* | *Iron (mg/100 ml of blood)* | | *Difference %* |
|---|---|---|---|
| | *EDTA analysis* | *o-Phenanthroline analysis* | |
| 1 | 43.7 | 44.4 | 1.6 |
| 2 | 37.3 | 37.0 | 0.8 |
| 3 | 48.1 | 49.0 | 1.8 |
| 4 | 47.0 | 46.2 | 1.7 |
| 5 | 50.7 | 51.8 | 2.1 |
| 6 | 48.0 | 47.2 | 1.7 |
| 7 | 37.5 | 37.3 | 0.5 |
| 8 | 40.9 | 40.4 | 1.2 |
| 9 | 41.1 | 40.2 | 2.2 |

TABLE II

REPRODUCIBILITY OF AUTOMATIC PROCEDURE

| *Sample No.* | *Iron (mg/100 ml of blood)* |
|---|---|
| 1 | 44.2 |
| 2 | 43.1 |
| 3 | 42.6 |
| 4 | 43.7 |
| 5 | 43.7 |
| 6 | 42.9 |
| 7 | 44.0 |
| 8 | 44.5 |
| Average | 43.6 |
| Standard deviation | 0.7 |

In Table III figures are given to show the recovery of iron, which has been added to 6 blood samples. The recovery of Fe varied from 96.9 to 103.5% with an average of 101.2%, whether the addition was made before or after ashing.

The volume of the solution in the 100-ml tall-form beaker is always adjusted to about 62–64 ml prior to titration to ensure the most efficient stirring without interference from air bubbles. The delivery rate of the titrant is adjusted carefully to about 5 ml/min — both for the standardization of the titrant and for the determination of iron — by varying the opening of the teflon stopcock and pinch-off valve.

At this rate a blank of 0.07 ml is applied, because of a slight but reproducible overshooting of the equivalence point.

EDTA usually contains up to about 0.3% absorbed moisture and for general purposes a sufficiently accurate solution may be obtained by weighing an appropriate amount, dissolving it and diluting to definite volume[6]. Therefore the standardization of titrant can be omitted, once a new bottle of EDTA has been checked for its purity. In such a case, in eqn. (1), $A = 0.56$.

TABLE III

RECOVERY OF IRON ADDED TO BLOOD

| *Sample No.* | *Iron (mg/100 ml of blood)* | | |
|---|---|---|---|
| | *Content* | *Added* | *Recovered* |
| 1 | 43.7 | 16.0 | 60.0 |
| 2 | 40.9 | 20.0 | 60.5 |
| 3 | 48.0 | 28.0 | 76.9 |
| 4 | 47.0 | 20.0 | 67.7 |
| 5 | 50.7 | 32.0 | 81.7 |
| 6 | 48.1 | 40.0 | 87.0 |

Calcium and magnesium do not interfere with the iron determination, because at pH values of about 4 their EDTA complexes are practically completely dissociated. Copper can be titrated with iron and cause a positive error. This error is not significant, however, because copper is present only in trace amounts (0.05–0.25 mg Cu/100 ml of blood).

## SUMMARY

A method is described for the determination of iron in blood which combines a rapid digestion procedure and automatic titration. The method is more rapid than conventional methods and as accurate. After wet ashing of the blood, an excess of standard EDTA is added, and back-titrated automatically with copper solution and Calcein W as indicator. The total time for a determination is about 15 min.

## RÉSUMÉ

Une méthode rapide de titrage automatique est proposée pour le dosage du fer dans le sang. On ajoute un excès d'EDTA qu'on titre avec une solution de cuivre en présence de calcéine comme indicateur.

## ZUSAMMENFASSUNG

Beschreibung einer raschen, automatischen Titrationsmethode zur Bestimmung von Eisen in Blut. Die Probe wird nass verascht, mit einem Überschuss von EDTA versetzt und der Überschuss mit einer Kupfersalzlösung und Calcein W als Indikator zurücktitriert.

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# DETERMINATION OF TRACES OF BISMUTH WITH DITHIZONE AFTER IODIDE EXTRACTION

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(Received April 2nd, 1961)

Earlier work[1] has shown that bismuth can be quantitatively extracted as $BiI_3$ with isoamyl acetate or isoamyl alcohol from aqueous solutions of low iodide concentration. The present report deals with the photometric determination of bismuth with dithizone after iodide extraction with isoamyl acetate from perchloric acid solution. After separation of the aqueous phase, the isoamyl acetate extract is shaken with an aqueous solution of dithizone in a buffer of pH 10.4–10.5 containing cyanide, sulfite, and citrate. A solution of bismuth dithizonate in isoamyl acetate is thus obtained, whose transmittance is measured at $\sim$480 m$\mu$. In this way, $\mu$g quantities of bismuth can be determined sensitively and relatively simply in samples containing much iron, calcium, magnesium, phosphate, etc. The method is not suitable for samples containing elements giving slightly soluble iodides, *i.e.*, Ag, Cu, Pb, Tl and Hg, although a few tenths of a mg of most of these can be tolerated.

This method was developed with application to natural materials in mind. Apparently, the bismuth content of igneous rocks is too low to allow determination by a photometric method on a $\sim$1-g sample. However, it appears that in sedimentary rocks bismuth may rise into the range where a sensitive photometric method can be of use. Because phosphate in large amounts does not hinder the extraction of bismuth iodide, the present method can be applied to phosphate rock and bone. Fluoride in considerable amounts — 25 mg, probably more — causes no difficulties. Chloride, except when present in low concentrations, impedes the iodide extraction of bismuth, but it, as well as much fluoride, can be expelled by evaporating to fuming with perchloric acid. Sedimentary rocks would in general be heated, before being brought into solution, to oxidize organic matter and sulfides. Mercury, which might otherwise interfere, would be eliminated in this step.

## DITHIZONE DETERMINATION

When an isoamyl acetate solution of bismuth iodide is shaken with an excess of a basic aqueous dithizone solution, pH 10.4–10.5, bismuth dithizonate is quantitatively formed in the organic phase. The excess dithizone partitions between the two phases, a considerable amount remaining in the isoamyl acetate. Fig. 1 shows that dithizone in this solvent exhibits absorption maxima at approximately 450 and 625 mμ. The maxima fall at very nearly the same wave lengths as in carbon tetrachloride solution (450 and 620 mμ), but the respective peak heights are reversed in the two solvents. Dithizone is present predominantly in the undissociated form in an isoamyl acetate solution in equilibrium with the basic aqueous solution; the possibility of a small fraction being present as dithizonate ion in the ester is not excluded. Bismuth dithizonate shows an absorption maximum at *ca.* 480 mμ in isoamyl acetate, close to the first maximum of dithizone. The difference between the extinction coefficients of bismuth dithizonate and dithizone and the preferential partitioning of the latter into the aqueous phase make a sensitive determination of bismuth possible. The sensitivity is 0.003 μg Bi/cm$^2$ for log $I_0/I = 0.001$ at 480 mμ.

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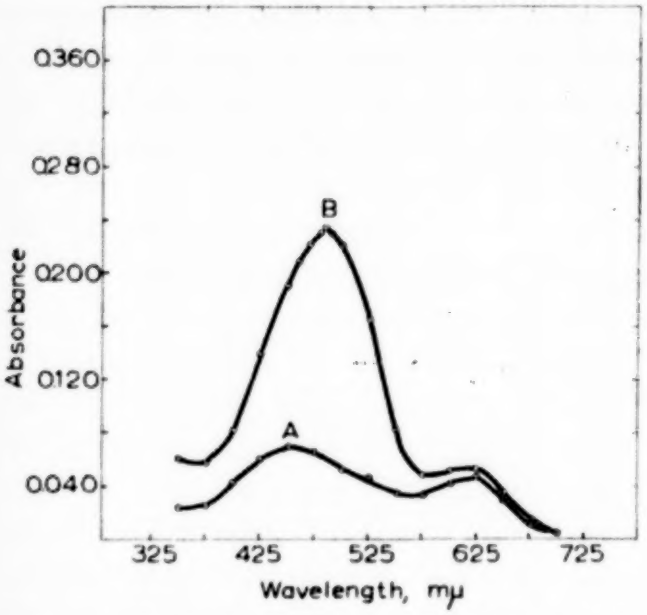

Fig. 1. Absorbance curves of dithizone (A) and bismuth dithizonate (B), 0.5 p.p.m. w/v Bi, in isoamyl acetate. 15 ml aqueous phase (pH 10.4) shaken with 10 ml of isoamyl acetate containing *ca.* 7.5 mg dithizone per l. Beckman B spectrophotometer, 1-cm cell.

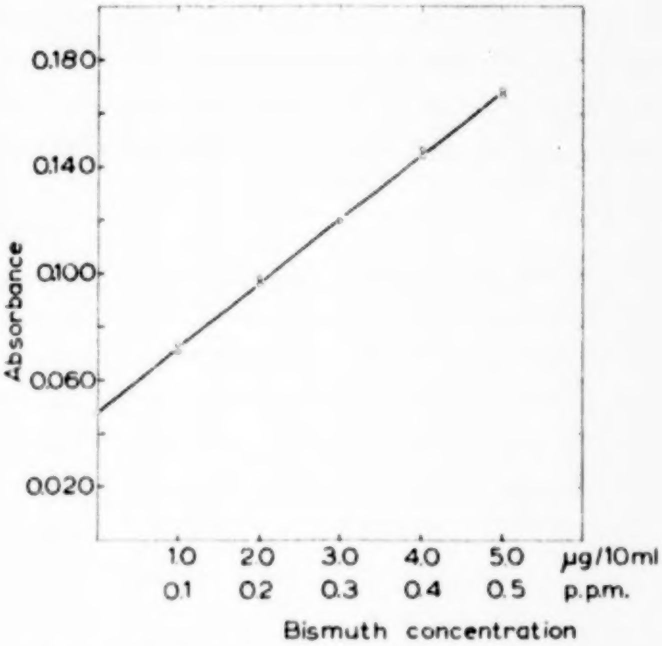

Fig. 2. Typical standard curve for determination of bismuth in isoamyl acetate (15 ml aqueous phase, 10 ml isoamyl acetate); 1-cm cell, 490-mμ filter. Original concentration of dithizone in aqueous phase 5 mg/l.

The optimum pH for the determination is close to 10.5. Above this pH the absorbance of a fixed amount of bismuth falls off rapidly. The absorbance is constant (after subtraction of the blank absorbance due to dithizone) in the pH range 10.5 to 9 or lower. It is advantageous to work at a pH of 10.4–10.5 in order to minimize the amount of dithizone in the isoamyl acetate. The bismuth absorbance is independent of the sulfite content (0.4 to 4% $Na_2SO_3$) and the cyanide content (0.3 to 2.5% $CN^-$) of the buffer, but it decreases with an increase in the citrate concentration. The use of an amount of dithizone equivalent to a 7.5 p.p.m. (w/v) isoamyl acetate solution permits the determination of as much as 5 μg Bi with acceptable precision. A typical standard curve obtained by the use of a filter photometer is reproduced in Fig. 2. The average deviation of an absorbance measurement corresponds to *ca.* 0.01 p.p.m. Bi, or 0.1 μg Bi in 10 ml of isoamyl acetate. The absorbance of a bismuth dithizonate solution in isoamyl acetate decreases slowly with time at room temperature in daylight. After 1 h, 0.3- and 0.5-p.p.m. Bi solutions showed a decrease of 3–4 % in absorbance.

## BEHAVIOUR OF OTHER ELEMENTS

The possible interference of lead must especially be considered because it may outweigh bismuth in natural samples by a factor of 10 or 100 if not more, and it reacts in the same manner as bismuth with dithizone in cyanide medium. Under the conditions of the procedure below, 1–2% of the total lead is extracted as iodide with isoamyl acetate. On washing with perchloric acid – iodide solution, the amount of lead in the organic solvent phase is reduced in like proportion, so that as much as 0.4 mg of lead in the original sample causes no sensible error. Thallium(I) is not extracted significantly as iodide and 0.1 mg Tl gives rise to no error. It is important

TABLE I

DETERMINATION OF BISMUTH AS DITHIZONATE FOLLOWING IODIDE EXTRACTION

| *Foreign elements* | *Bi taken* µg | *Bi found* µg |
|---|---|---|
| | 1.0 | 0.8, 0.9, 0.9 |
| | 2.0 | 1.9, 2.0, 1.9, 2.0 |
| | 4.0 | 3.8, 3.8 |
| | 5.0 | 5.0, 4.9, 4.9 |
| Pb, 0.1 mg | 1.0 | 1.0, 0.9 |
| Pb, 0.4 mg[a] | 0 | 0.0, 0.0 |
| Pb, 0.4 mg | 1.0 | 1.0, 0.9, 1.0 |
| Pb, 0.4 mg | 4.0 | 3.9, 3.8, 4.0 |
| Tl(I), 0.05 mg | 2.0 | 2.0, 2.0 |
| Tl(I), 0.10 mg | 2.0 | 2.1, 2.1 |
| In(III), 0.10 mg | 4.0 | 4.0, 4.0 |
| Cd, 0.1 mg | 2.0 | 2.0, 2.0 |
| Cu(II), 0.5 mg | 4.0 | 4.0, 3.9 |
| Sn(II), 0.5 mg | 5.0 | 4.9, 5.0 |
| As(V), 0.5 mg | 5.0 | 4.9, 5.0 |
| Sb(III), 0.5 mg | 1.0 | 0.9, 0.9 |
| Sb(III), 0.5 mg | 2.0 | 1.9, 2.0 |
| Hg(II), 0.01 mg | 2.0 | 2.1, 1.9 |
| Hg(II), 0.01 mg | 4.0 | 3.8, 4.0 |
| Hg(II), 0.10 mg | 1.0 | 0.7, 0.8 |
| Hg(II), 0.10 mg[b] | 2.0 | 1.8, 1.9 |
| Ag, 0.1 mg | 4.0 | 4.1, 4.0 |
| Ti(IV), 20 mg | 2.0 | 1.9, 1.8 |
| V(V), 10 mg | 5.0 | 4.9, 4.9 |
| $Cl^-$, 10 mg | 3.0 | 2.9, 2.9 |
| $F^-$, 25 mg | 4.0 | 3.9, 4.0 |
| $CNS^-$, 12 mg | 2.0 | 2.0, 1.9 |
| Fe(III), 100 mg | 3.0 | 3.0, 2.9, 3.0 |
| $Ca_3(PO_4)_2$, 1000 mg | 5.0 | 4.9, 5.0 |
| $Ca_3(PO_4)_2$, 500 mg; $Mg_3(PO_4)_2$, 500 mg; Pb, 0.4 mg | 4.0 | 4.0, 4.1, 4.1 |
| Fe(III), 100 mg; $PO_4$, 600 mg | 2.0 | 2.1, 2.0 |
| Fe(III), 50 mg; Al, 50 mg[c]; $PO_4$, 600 mg | 2.0 | 2.0, 2.0, 1.9 |

[a] This is approximately the permissible upper limit for Pb. With 0.5 mg Pb, a precipitate of $PbI_2$ appears.

[b] Solution made 0.02 *M* in NaSCN before iodide extraction.

[c] Al added as nitrate; result shows that as much as 350 mg $NO_3^-$ does not hinder extraction of bismuth iodide.

that free iodine not be present in the iodide extraction, for some thallium(III) will then enter the isoamyl acetate phase. The amounts of lead and thallium must be such that no appreciable iodide precipitate is formed. Such a precipitate will gather at the isoamyl acetate – water interface and may survive the back-washing, and thus cause serious error. Tin(II) and indium, which can also react with dithizone in basic medium, do not interfere.

Mercury leads to low results for bismuth, even in amounts as small as 0.1 mg (Table I). Addition of thiocyanate before the iodide extraction prevents the interference of such amounts of mercury, but in applied analysis, as already mentioned, mercury will be volatilized in the preliminary heating of the sample and the use of thiocyanate is unnecessary.

Most other elements, including titanium, vanadium, arsenic, antimony, and cadmium do not interfere, at least not in the amounts that they may be expected to occur in materials for which the method is intended. Ferric iron must be reduced to the ferrous state, which can be done effectively with sulfite and ascorbic acid. As much as 0.1 g of iron(III) can be made harmless in this way. The high acidity of the solution — 2 *N* in perchloric acid — from which the bismuth iodide extraction is made permits the presence of much phosphate. The use of perchloric acid avoids the precipitation of calcium sulfate. Sulfuric acid probably can be used for acidification when the alkaline earth elements are absent.

## REAGENTS

### *Isoamyl acetate*

Wash a reagent-quality product with three portions of an aqueous solution 1% in sodium hydroxide and 1% in sodium sulfite, using about 1/5 as much aqueous solution as ester. Wash once or twice with water. Distil the isoamyl acetate in the presence of benzene (10 ml for 250–300 ml of ester) to remove water. Collect the fraction boiling between 137–142°.

### *Sodium iodide*

2.1 g in 100 ml water (0.14 *M*).

### *Buffer–cyanide solution*

Dissolve 20 g of diammonium citrate, 10 g of sodium sulfite, and 30 g of potassium cyanide in 800 ml of water. Add ammonia to give a pH of about 9 and shake with small portions of 0.02% dithizone in carbon tetrachloride to remove lead. Remove most of the dithizone by shaking with carbon tetrachloride. Adjust the pH to 10.5 by adding pure ammonium hydroxide and dilute to 1 l with water. Store in a polyethylene bottle.

### *Stock dithizone solution, 0.010% (w/v)*

Dissolve 10 mg of dithizone of adequate purity in 100 ml of the buffer–cyanide solution. Store the solution in a refrigerator. It should show little change in strength in two weeks time.

### *Standard dithizone solution, 0.0005% (w/v)*

Shortly before use, dilute 5.00 ml of the stock dithizone to 100 ml with the buffer-cyanide solution.

*Standard bismuth solution*

Prepare a stock solution by dissolving bismuth metal (>99.5%) in nitric acid and diluting to obtain a 0.1% Bi solution in 1 *N* nitric acid. Immediately before use dilute this solution to 0.001% Bi with water.

## PROCEDURE

The sample solution may contain up to 5 µg Bi; possible interfering elements must be within the limits mentioned in the preceding discussion. Add enough perchloric acid to make its concentration 2.0 *N* after dilution to 20 ml. Dilute with water to within 1–2 ml of 20 ml and add 0.8 g sodium sulfite ($Na_2SO_3$), 0.4 g ascorbic acid and 1.00 ml of sodium iodide solution. Allow to stand until any free iodine has been reduced.

Extract with two 5.00-ml portions of isoamyl acetate, shaking for 3 min each time. Combine the extracts and shake with 10 ml of aqueous solution containing 0.4 g sodium sulfite, 0.2 g ascorbic acid and 0.50 ml of 0.14 *M* sodium iodide solution, and which is 2 *N* in perchloric acid (*i.e.* the same composition as the solution from which bismuth is extracted).

Draw off the aqueous phase sharply and shake the isoamyl acetate phase with 15.0 ml of standard dithizone solution for 1 min. Discard the aqueous layer and run the isoamyl acetate through a small plug of glass wool into a 1-cm absorption cell. Obtain the absorbance within 10 min at 480 (470–490) mµ, with isoamyl acetate in the reference cell.

Establish the standard curve by taking 0, 1, 2, 3 and 4 µg Bi, adding 15.0 ml of standard dithizone solution, shaking for 1 min with 10.0 ml of isoamyl acetate, and obtaining the absorbance of the extract.

## ACKNOWLEDGEMENT

One of the writers, H. A. M., wishes to express his thanks to the University of Buenos Aires, Argentina, for a fellowship held during the course of this work.

## SUMMARY

A method for the determination of µg quantities of bismuth in the presence of much iron, calcium, magnesium and phosphate is described. Bismuth is extracted as $BiI_3$ by isoamyl acetate from perchloric acid medium in the presence of ascorbic acid and sulfite, and determined as dithizonate in the isoamyl acetate phase. The method is intended particularly for natural materials such as silicates and phosphates in which bismuth exceeds a few tenths of a p.p.m. and lead is present in amounts below 500 p.p.m.

## RÉSUMÉ

Une méthode est décrite pour le dosage de traces de bismuth, en présence de fortes concentrations de fer, calcium, magnésium et phosphate. Le bismuth est extrait sous forme de $BiI_3$ par l'acétate d'isoamyle en milieu perchlorique, en présence d'acide ascorbique et de sulfite, et dosé comme dithizonate.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Wismut neben viel Eisen, Calcium, Magnesium und Phosphat. Das Wismut wird als $BiI_3$ mit Isoamylacetat extrahiert und als Dithizonat bestimmt.

## REFERENCE

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# LIQUID-LIQUID EXTRACTION OF IRON(III) WITH 2-THENOYLTRIFLUOROACETONE FROM A NITRATE SYSTEM, AND DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

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(Received April 15th, 1961)

2-Thenoyltrifluoroacetone (TTA) extracts many metallic ions from different media[1-4]: the majority of these metallic ions give coloured chelates with TTA which can sometimes be directly determined by means of a colorimetric method[5-7].

**Khopkar and De**[7] have determined iron(III) in the organic phase ($\lambda = 460$ m$\mu$) after extraction at pH 2 with 0.15 $M$ TTA. This rapid and accurate method, when generally applied, presents the limitation that under the reported conditions several metallic ions can also be extracted if present with iron, so that poor results are obtained. In fact these authors report that Ag(I), Cu(II), Mn(II), Ni(II), Hg(II), Bi(III), Al(III), Ce(IV), Th(IV), Zr(IV) and V(V) seriously interfere in the colorimetric determination. Furthermore, at pH 2, it is sometimes very difficult to bring into solution great quantities of metallic ions. For these reasons we have considered the paper by **Moore** *et al.*[4] who shows that about 90% of iron(III) is very selectively extracted by 0.5 $M$ TTA from a 10$M$ nitric acid solution, and a red chelate compound is formed. However, to get dependable and rapid colorimetric results it is necessary to extract iron quantitatively: therefore, in the present work we have studied the possibility of achieving the quantitative extraction of iron followed by its determination by organic phase colorimetry.

## EXPERIMENTAL

### *Reagents*

Iron, as iron nitrate, was dissolved in 4 $M$ nitric acid in order to have a solution containing 200 $\mu$g of iron per ml, which was then controlled with 0.01 $M$ EDTA. Nitric acid and ammonium nitrate solutions were completely purified from iron by means of extractions with TTA. TTA solutions were obtained by dissolving the desired quantity of TTA (supplied by Fluka) in xylene. All the other chemicals used were reagent grade materials; $^{59}$Fe was supplied by Harwell.

### *Apparatus*

A Spectrophotometer Coleman Universal Mod. 14 with 13-mm cells was used for absorbance measurements. The shaker was a special type with a rapid wrist motion: extractions at controlled temperatures were obtained by shaking the 50-ml flasks in beakers containing water coming from a thermostat. The counting of $^{59}$Fe was performed by a Geiger-Müller liquid counter (SBL. CISE).

*Absorption curves*

As illustrated in Fig. 1, the absorption spectrum of 0.5 *M* TTA–xylene pre-equilibrated with 10 *M* nitric acid shows a simple peak at 400 m$\mu$, whereas the absorption spectrum of the chelate 0.5 *M* TTA iron(III) shows one peak at 430 m$\mu$ and one inflection at about 510 m$\mu$. Although the extraction conditions reported by KHOPKAR AND DE[7] are very different from ours, the shape of the absorption spectrum was very similar.

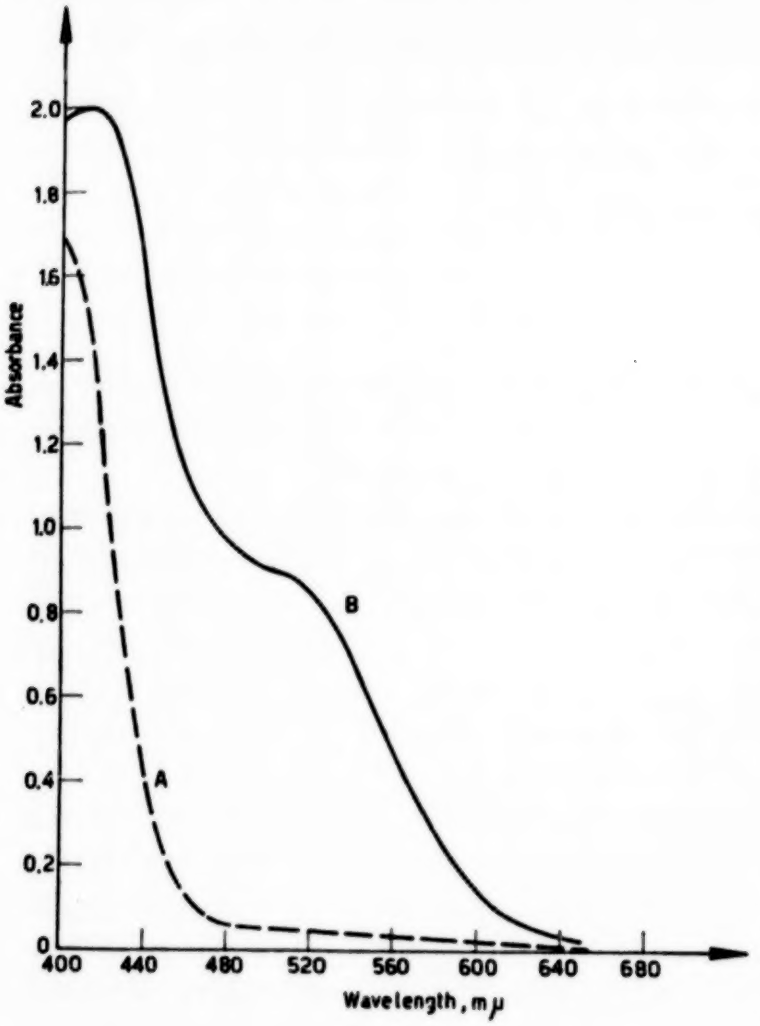

Fig. 1. Absorption spectra. A: 0.50 *M* TTA pre-equilibrated with 10 *M* $HNO_3$, against xylene. B: Iron(III)–TTA 0.50 *M* against xylene. Extraction of 100 $\mu$g iron from 10 *M* $HNO_3$ with 10 ml TTA 0.50 *M*.

TABLE I

| *Iron taken* $\mu$*g* | *Absorbance of the organic phase at 510 m*$\mu$ |
|---|---|
| 2 | 0.018 |
| 5 | 0.047 |
| 10 | 0.094 |
| 25 | 0.232 |
| 50 | 0.460 |
| 100 | 0.920 |
| 200 | 1.700 |

In the present work we have chosen the wavelength of 510 m$\mu$ at which TTA shows a negligible absorbance. In order to check, for this particular case, the linearity between the iron concentration and its absorbance, 2 to 200 $\mu$g of iron dissolved in 10 ml of 10 *M* nitric acid was extracted with 10 ml of 0.5 *M* TTA: after shaking for 10 min at room temperature (22° ± 1°), the absorbance of the organic phase was measured at 510 m$\mu$ against a reagent blank. Table I shows that a linear relationship holds over a wide range of iron concentration. However, a second extraction confirmed that 10% of the total iron remained in the inorganic phase.

*Extraction studies*

To obtain a quantitative iron extraction from a nitric medium we have considered the following variables: (*a*) TTA concentration, (*b*) nitric acid and ammonium nitrate concentration, (*c*) extraction time, (*d*) extraction temperature. As sometimes[8,9] anionic complexes form more easily in an ammonium nitrate than in a nitric acid medium, we performed some iron extraction also from 10 *M* ammonium nitrate solutions and with different TTA concentrations.

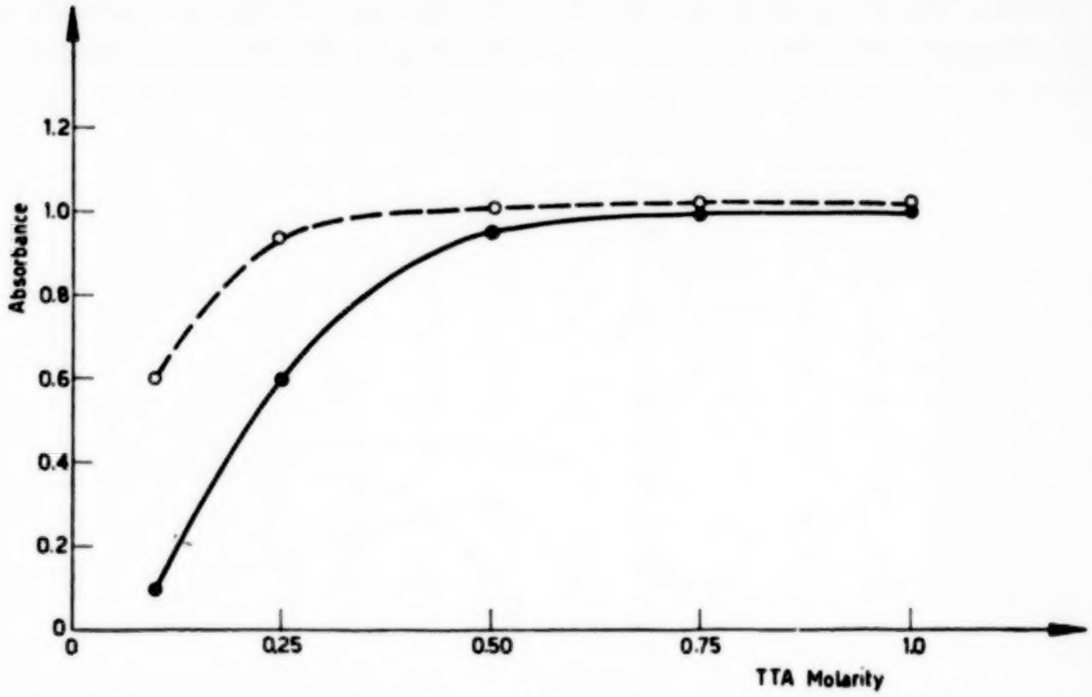

Fig. 2. Iron(III) extraction as a function of TTA molarity. 30-min extraction from 10 *M* $HNO_3$ (solid line), and from 10 *M* $NH_4NO_3$ (dashed line). The absorbance of the organic phase was measured against a reagents blank at 510 m$\mu$.

The results we obtained are illustrated in Figs. 2 and 3, which clearly show that, after a long shaking time, the iron extraction from 10 *M* ammonium nitrate is greater than that from 10 *M* nitric acid, especially with low TTA concentrations. The equilibrium is quickly reached with nitric acid and very slowly with ammonium nitrate; in both cases the concentration has a great influence on iron extraction. All these extraction experiments were performed by shaking 10 ml of inorganic solution con-

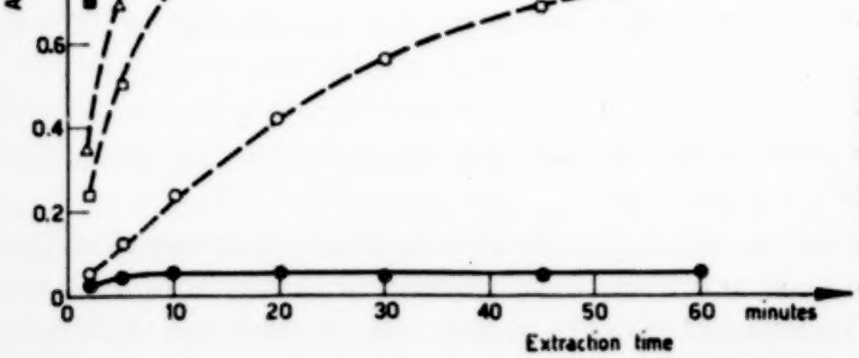

Fig. 3. Effect of shaking time and TTA molarity on iron(III) extraction. ●, 0.10 *M* TTA and 10 *M* $HNO_3$; ⊙, 0.1 *M* TTA and 10 *M* $NH_4NO_3$; ■, 0.50 *M* TTA and 10 *M* $HNO_3$; □, 0.50 *M* TTA and 10 *M* $NH_4NO_3$; ▲, 0.78 *M* TTA and 10 *M* $HNO_3$; △, 0.78 *M* TTA and 10 *M* $NH_4NO_3$.

taining 100 µg iron with 10 ml of TTA–xylene at room temperature (22° ± 1°); the absorbance of the organic phase was determined at 510 mµ.

The results obtained show that 10 ml of 0.78 *M* (15%) TTA quantitatively extracts 100 µg of iron 10 *M* ammonium nitrate after shaking for 60 min: in this case a second extraction did not show any trace of iron remaining in the inorganic phase.

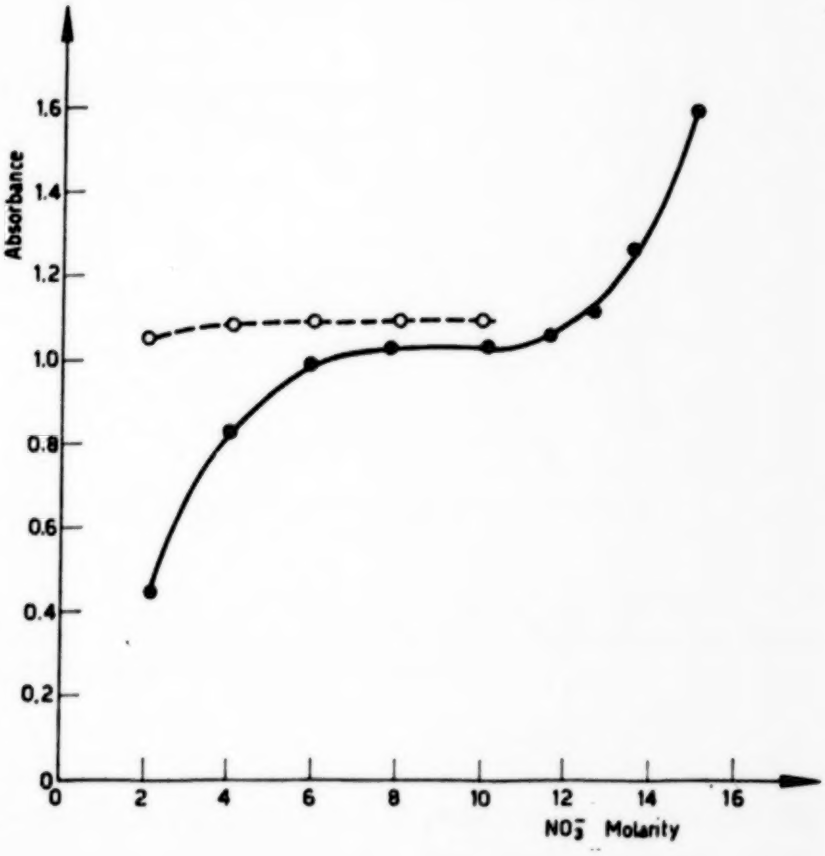

Fig. 4. Iron(III) extraction as a function of nitrate molarity. $HNO_3$, solid line; $NH_4NO_3$, dashed line. Shaking times: 15 min for $HNO_3$ and 60 min for $NH_4NO_3$; 100 µg iron, 0.78 *M* TTA (10 ml).

Nitric acid added to 8 *M* ammonium nitrate improves the attainment of the equilibrium when the extraction times are short (10 min), but it does not influence the already quantitative iron extraction when the extraction time is long (60 min).

Fig. 4 illustrates the iron extraction, at the equilibrium, as a function of the nitric acid and ammonium nitrate molarity. As already reported by MOORE *et al.*[4], the use of nitric acid concentration higher than 11–12 *M* degrades TTA, lowering the iron extraction: therefore in this case the strong absorption we have measured is not proportional to the iron extraction, but depends also on TTA degradation.

In order to study iron extraction with greater accuracy and independently of the organic phase absorbance, we used iron-59 as a tracer, counting the inorganic phase after extraction.

Fig. 5 shows the extraction coefficients ($E_a{}^\circ$) determined by the tracer method as functions of nitric acid and ammonium nitrate molarity: the degradation of TTA is clear when the nitric acid concentration is greater than 12 *M*, which results in decreased extraction coefficients.

Fig. 6 shows the influence of shaking time on the extraction coefficients when 10 *M* ammonium nitrate and 0.78 *M* TTA are used.

In order to shorten the time for equilibrium attainment, some experiments of iron extraction from ammonium nitrate solutions were performed at higher than room temperature. The extraction coefficients become greater and greater for 10 *M* ammonium nitrate and decrease slightly for 10 *M* nitric acid, after a 10-min extraction at temperatures increasing from 20° to 47°. This different behaviour can be explained considering that for the slowly reactive ammonium nitrate solutions a high temperature can shorten the time required to attain an equilibrium which is very slow at room temperature, whilst for the highly reactive nitric acid solutions it can only increase the TTA degradation, without influencing the equilibrium which is already very rapid at room temperature. In fact, with nitric acid solutions the two phases appeared very turbid at temperatures higher than 25°, whilst this did not happen when 10 *M* ammonium nitrate solutions were used.

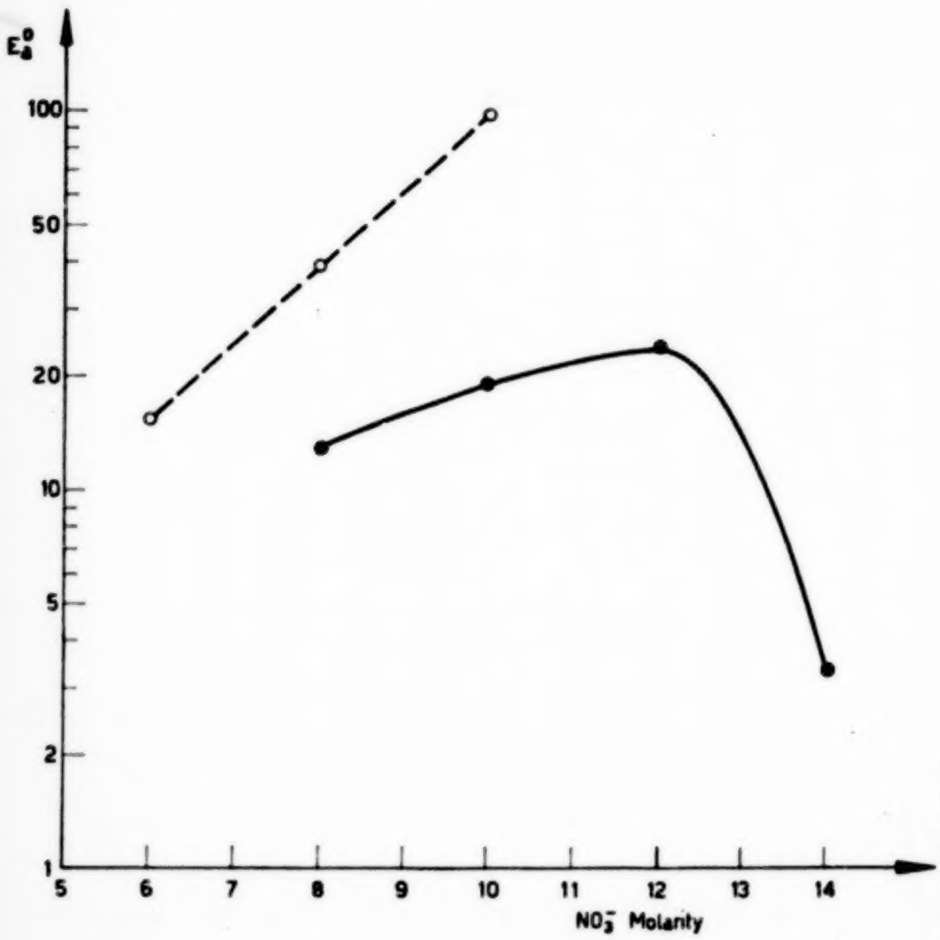

Fig. 5. Extraction coefficients ($E_a^0$) as a function of nitrate molarity. $HNO_3$, solid line; $NH_4NO_3$, dashed line. Shaking time: 30 min, TTA 0.78 *M*; 100 µg iron + $^{59}Fe$ as a tracer.

In any case, it is clear that extraction is quantitative ($E_a^0 = 200$) by extracting iron from 10 *M* ammonium nitrate solutions with 15% TTA and with a 10-min shaking at temperatures between 40° and 50°.

However, in many practical cases a certain quantity of free nitric acid is necessarily added in order to dissolve considerable amounts of salts: therefore some iron extractions were performed by using 2 *M* nitric acid and 9 *M* ammonium nitrate solutions, and once again an iron extraction >99.5% was obtained.

### *Calibration curve and recommended procedure*

The calibration curve was obtained in the following way: 10 ml of the 2 *M* nitric acid–9 *M* ammonium nitrate solution containing 2 to 100 µg of iron were shaken in a 50-ml flask with exactly 10 ml of 15% TTA–xylene for 10 min at 45° ± 1°. After separating the phases in a separatory funnel, the organic phase was directly measured at 510 mµ against a reagent blank.

The calibration curve, which is a straight line within 0 and 100 μg of iron, yields a molar extinction coefficient equal to 4900 ± 100 at 510 mμ. This figure is very similar to that found by KHOPKAR AND DE[7] (4880 ± 61) at 460 mμ. The colour is stable for many hours.

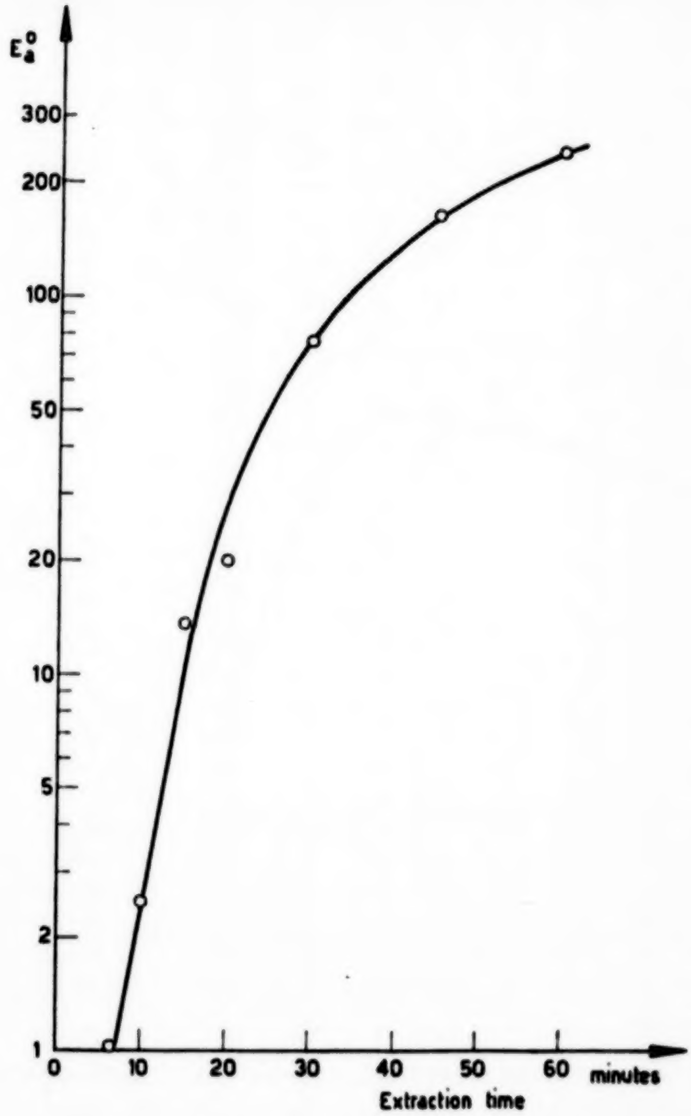

Fig. 6. Extraction coefficients ($E_a^\circ$) of iron(III) as a function of shaking time. 0.78 $M$ TTA, 10 $M$ $NH_4NO_3$, 100 μg iron + $^{59}Fe$ as a tracer.

### *Interfering ions*

The majority of metallic ions are not extracted with TTA from the 2 $M$ nitric acid–9 $M$ ammonium nitrate solution, and therefore do not cause false colorimetric results.

Among the metallic ions we have tested, only zirconium(IV) and cerium(IV) can be extracted, but zirconium chelate is not coloured and, if in low amounts, does not interfere with the iron colorimetry.

Cerium(IV) chelate is red and seriously interferes: moreover in the nitric medium cerium(III) is partially oxidized to cerium(IV) causing interferences as well. As Table II shows, 100 μg of iron were added with 20 mg of different metallic ions: the results were accurate within ±2%, except for cerium(IV) and cerium(III). Large quantities of chloride and sulphate ions also interfere by lowering iron extraction.

## ANALYSIS OF IRON IN METALS

### *Determination of iron in uranium*

The described procedure can be usefully applied to the determination of iron in uranium. 1 g of metallic uranium was dissolved by means of 20 ml of concentrated nitric acid: after evaporating the excess of acid, the solid uranium nitrate was dissolved in 20 ml of 10 *M* nitric acid and purified from iron by means of three extractions with 15% TTA at room temperature.

TABLE II

(100 μg of iron(III) + 20 mg of several ions)

| *Ion (20 mg)* | *Added as* | *Remarks* |
|---|---|---|
| Na(I) | $NaNO_3$ | No interference |
| Ag(I) | $AgNO_3$ | No interference |
| Ca(II) | $CaCl_2 \cdot 6\ H_2O$ | No interference |
| Co(II) | $CoCl_2 \cdot 6\ H_2O$ | No interference |
| Cu(II) | $CuSO_4 \cdot 5\ H_2O$ | No interference |
| Ni(II) | $NiSO_4 \cdot 7\ H_2O$ | No interference |
| Hg(II) | $HgCl_2$ | No interference |
| Mn(II) | $MnCl_2 \cdot 4\ H_2O$ | No interference |
| Bi(III) | $Bi(NO_3)_3 \cdot 5\ H_2O$ | No interference |
| Cr(III) | $CrCl_3 \cdot 6\ H_2O$ | No interference |
| Al(III) | $AlCl_3 \cdot 6\ H_2O$ | No interference |
| La(III) | $La(NO_3)_3 \cdot 6\ H_2O$ | No interference |
| Ce(III) | $Ce(NO_3)_3 \cdot 6\ H_2O$ | Interference |
| Ce(IV) | $Ce(SO_4)_4 \cdot 4\ H_2O$ | Interference |
| Th(IV) | $Th(NO_3)_4 \cdot 4\ H_2O$ | No interference |
| Zr(IV) | $ZrOCl_2 \cdot 8\ H_2O$ | No interference |
| U(VI) | $UO_2(NO_3)_2 \cdot 6\ H_2O$ | No interference |

The uranium nitrate solution, thus purified from iron, was then mixed with 50 μg of iron, and after the evaporation of nitric acid, the solid uranium nitrate was dissolved in 20 ml of the 2 *M* nitric acid–9 *M* ammonium nitrate solution and transferred quantitatively to a 50-ml flask. After a 10-min extraction at 45° with 10 ml of 15% TTA, the organic phase absorbance was measured in the usual way: from the calibration curve a value of 51 μg of iron was found.

### *Determination of iron in cobalt*

To 1 g of cobalt, which had been previously purified from iron in the same way as uranium, 80 μg of iron were added. After dissolution of the solid cobalt nitrate in 20 ml of the 2 *M* $HNO_3$–9 *M* $NH_4NO_3$ solution, iron was extracted at 45° and determined as usual: 80.4 μg of iron were found.

### *Determination of iron in aluminium*

An amount of 0.5 g of aluminium, as nitrate, was dissolved in 1 : 1 hydrochloric acid and purified from iron by means of two extractions with 0.1 *M* tri-*n*-octylamine (TNOA); after the addition of 40 μg of iron, hydrochloric acid was first evaporated and then completely eliminated with iron-free 10 *M* nitric acid. Finally the solid aluminium nitrate was dissolved in 20 ml of the usual solution: the procedure was completed as usual with a result of 40.5 μg.

### *Determination of iron in nickel in the presence of HCl*

*Example of differential analysis.* 2 g of nickel, as nitrate, were dissolved in 1 :1 hydrochloric acid and purified from iron approximately as described for aluminium.

After the addition of 100 µg of iron, the hydrochloric acid was evaporated and nickel chloride was dissolved in exactly 25 ml of 2 $M$ $HNO_3$–9 $M$ $NH_4NO_3$ solution: in this case the final solution was 2.5 $M$ in hydrochloric acid, which is said to lower the iron extraction. In fact, from the calibration curve we found only 88% of the added iron, but a good result was obtained by means of a differential analysis. This type of analysis consists in adding different known quantities of iron to some samples of the original solution before extraction. This method gives more accurate results and also eliminates any possible interference.

## CONCLUSIONS

The results obtained show that TTA extracts iron quantitatively from concentrated ammonium nitrate solutions and also in the presence of some nitric acid. Furthermore it is possible to determine iron directly in the organic phase. The method appears to be very selective, and a few µg of iron can be determined in the presence of large amounts of several metallic ions.

## ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Prof. E. Cerrai for helpful suggestions, and to recognize the accurate work done by M. G. Ranzini in this study.

## SUMMARY

Iron extraction with TTA from concentrated nitric acid and ammonium nitrate solutions is considered with regard to reagent concentrations and the time and temperature of extraction. It is possible to determine 0.2 to 10 µg/ml of iron directly in the organic phase by measuring its absorbance at 510 mµ. Large amounts of several metallic ions can be present, *e.g.* iron can be determined in U, Co, Al, Ni.

## RÉSUMÉ

Les auteurs décrivent une extraction du fer(III) au moyen de 2-thénoyltrifluoroacétone, permettant un dosage colorimétrique de cet élément, directement dans la phase organique. On a pu ainsi déterminer des teneurs en fer de 0.2 à 10 µg/ml, en présence de nombreux ions métalliques, même en fortes proportions, (dosage du fer dans l'uranium, dans le cobalt, dans l'aluminium, dans le nickel).

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Eisen in Gegenwart von z.B. Uran, Kobalt, Aluminium, Nickel durch Extraktion mit 2-Thenoyltrifluoroaceton und direkte colorimetrische Bestimmung in der organischen Phase.

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# DIE OXYDIMETRISCHE BESTIMMUNG VON EINWERTIGEM THALLIUM MIT Pb(IV)-AZETAT

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(Eingegangen den 27. April, 1961)

Zur massanalytischen Bestimmung von Thallium wurde eine Reihe von oxydations–reduktions Methoden vorgeschlagen, bei denen das einwertige Thallium entweder direkt mit einem geeignetem oxydimetrischen Reagens titriert wird, oder wird (nach vorgehender Oxydation) das dreiwertige Thallium mit einem reduktometrischen Reagens titriert. Einfacher durchzuführen sind die oxydimetrischen Bestimmungen, bei denen als oxydimetrisches Reagens z.B. Permanganat[1-3], Cerisulphat[4,5], Bromat[6-8], N-Bromsukcinimid[9], Hypobromit[10], Kaliumperjodat[11] u.a. zur Anwendung gelangen.

In der vorliegenden Arbeit haben wir die Möglichkeit der Titration von Lösungen von einwertigem Thallium mit Pb(IV)-Azetat untersucht, mit dessen Verwendung als oxydimetrischen Reagens zur Bestimmung von anorganischen Systemen in geeignet angesäuerten wässerigen Lösungen wir uns schon in einigen früheren Arbeiten[12-14] befasst haben. Wir haben gefunden, dass das einwertige Thallium mit Pb(IV)-Azetat durch direkte potentiometrische Titration in mit Chlorwasserstoffsäure angesäuerten Lösungen mit grosser Genauigkeit bestimmt werden kann. Da die Tl(I)-Salze in reinem Zustande als Standarde dienen, kann die ausgearbeitete Methode zur Bestimmung des Faktors des massanalytischen Reagens angewandt werden, insbesondere bei Titrationen im Mikromasstab.

## EXPERIMENTELLER TEIL

### *Reagentien*

Chlorwasserstoffsäure, Essigsäure (p.a. Lachema). Die für die Mikrobestimmungen verwendete Chlorwasserstoffsäure wurde durch Destillation einer azeotropen Mischung oder durch isothermale Diffusion nach ABRAHAMCZIK[15] gereinigt.

Eine 0.1 *N* Pb(IV)-Azetat Lösung in Eisessigsäure (frei von zweiwertigem Blei) wurde durch Reaktion von Minium mit Eisessigsäure bereitet[13] und der Faktor der Lösung durch Titration von Hydrazinsulphat bestimmt[12]. Eine 0.01 *N* Pb(IV)-Azetat Lösung wurde durch Verdünnen der 0.1 *N*-Lösung mit Eisessigsäure erhalten. Ihr Faktor wurde durch Titration von Eisen(II)-Sulphat kontroliert, dessen Faktor seinerseits mit Bichromat bestimmt wurde[16]. Eine 0.2 *N* Thallium(I)-Sulphatlösung wurde durch Lösen von 25.242 g $Tl_2SO_4$ (p.a. Lachema) in destilliertem Wasser bereitet und auf 1 l aufgefüllt. 0.08 *N*, 0.01 *N*, 0.0005 *N* und 0.0001 *N* Lösungen wurden durch genaue Verdünnung der 0.2 *N* Lösung mit destilliertem Wasser bereitet.

### *Apparatur*

Die potentiometrischen Titrationen wurden mit einem Elektronenröhren-pH-Meter EK/21 (Kovodružba, Praha) durchgeführt. Die Indikationselektrode war Platin, die Referenzelektrode war eine gesättigte Kalomelelektrode. (Alle weiterhin angegeben Potentiale sind in Bezug auf die gesättigte Kalomelelektrode angegeben). Zum Mischen der Lösungen wurde ein elektromagnetisches Rührwerk angewandt. Zum Abmessen der Lösungen wurden geeichte Messgefässe verwendet. Zur Titration wurden Büretten von 25 ml Volumen verwendet, zu 0.1 ml geteilt, und ferner Büretten von 5 und 1 ml Inhalt, zu 0.01 ml geteilt. Die Mikrobürette der Marke "Agla" hatte einen Inhalt von 0.5 ml und Teilungen zu 0.0002 ml.

## ÜBERSICHT DER RESULTATE

### *Semimikrobestimmung von Thallium*

Bei Versuchen um die direkte potentiometrische Titration von einwertigem Thallium mit Pb(IV)-Azetat haben wir gefunden, dass die Oxydation von Tl(I) zu Tl(III) mittels dieses Reagens am besten in mit Chlorwasserstoffsäure angesäuerten Lösungen verläuft. Während z.B. im Medium von Schwefelsäure die Oxydation von einwertigem Thallium nur schwierig und langsam verläuft, war es möglich im Medium von Chlorwasserstoffsäure das Thallium mit Pb(IV)-Azetat schon bei Laboratoriumstemperatur direkt potentiometrisch zu titrieren.

TABELLE I

TITRATION VON Tl(I) MIT 0.1 $N$ $PbAc_4$ IN EINEM MEDIUM VON 5–10 $N$ HCl

(8.18–102.19 mg Tl; Volumen = 50 ml)

| *Gegeben (mg)* | *Gefunden (mg)* | *Abweichung (%)* | *Potenzialänderung im Equivalenzpunkt* | *Inflexions potenzial* | *Konzentration HCl (N)* |
|---|---|---|---|---|---|
| 8.18 | 8.17 | —0.12 | 355[a] | 620 | 5 |
| 8.18 | 8.15 | —0.37 | 330[a] | 610 | 5 |
| 8.18 | 8.20 | +0.24 | 280[a] | 600 | 8 |
| 8.18 | 8.15 | —0.37 | 300[a] | 605 | 8 |
| 8.18 | 8.10 | —0.98 | 280[a] | 580 | 10 |
| 40.88 | 40.78 | —0.24 | 275[b] | 630 | 5 |
| 40.88 | 40.93 | +0.12 | 285[b] | 600 | 5 |
| 40.88 | 40.91 | +0.07 | 280[b] | 595 | 8 |
| 40.88 | 40.86 | —0.05 | 270[b] | 580 | 8 |
| 40.88 | 40.97 | +0.22 | 290[b] | 580 | 10 |
| 40.88 | 40.84 | —0.10 | 260[b] | 570 | 10 |
| 61.32 | 61.37 | +0.08 | 230[b] | 580 | 8 |
| 61.32 | 61.22 | —0.16 | 220[b] | 590 | 8 |
| 61.32 | 61.41 | +0.15 | 180[b] | 570 | 10 |
| 61.32 | 61.28 | —0.06 | 190[b] | 565 | 10 |
| 102.19 | 101.92 | —0.26 | 190[b] | 590 | 8 |
| 102.19 | 102.10 | —0.09 | 200[b] | 620 | 8 |
| 102.19 | 102.01 | —0.18 | 170[b] | 545 | 10 |
| 102.19 | 102.30 | +0.11 | 160[b] | 560 | 10 |

[a] Für 0.005 ml Massreagens

[b] Für 0.01 ml Massreagens

Der Verlauf der Titration wird durch die Konzentration von Chlorwasserstoffsäure in der Lösung beeinflusst. Bei ihrer niedrigeren Konzentration ensteht nämlich ein Niederschlag von Tl(I)-Chlorid, der bei höherer Chlorwasserstoffsäurekonzentration unter Bildung von Tl(I)-Chlorokomplexen gelöst wird. Das Entstehen der Komplexe bedingt den glatten Verlauf der Titration. Wir haben gefunden, dass bei der massanalytischen Bestimmung von 8–41 mg Tl mit 0.1 *N* Pb(IV)-Azetat in einem Anfangsvolumen von 50 ml die Titration in 5 bis 10 *N* HCl gut verläuft, während bei der Titration von 41–102 mg Tl zum glatten Verlauf der Titration die Konzentration der Chlorwasserstoffsäure 8 bis 10 *N* sein muss. Unter diesen Bedingungen wird der vor Anfang der Titration eventuell entstandene Niederschlag von Tl(I)-Chlorid während der Titration gelöst, ohne dass das Resultat der Titration unvorteilhaft beeinflusst werde. Für die Reaktionsgeschwindigkeit und die Grösse der Potentialänderung im Equivalenzpunkt zeigte sich uns ein Medium von 8 *N* HCl für die untersuchte Thalliummenge (8 bis 102 mg Tl in 50 ml) als optimal. Unter diesen Bedingungen verläuft die Potenzialstabilisation während der ganzen Titration augenblicklich, die Potenzialänderung im Equivalenzpunkt ist bedeutend und die Resultate sind nur mit sehr kleinen Fehlern behaftet. Die Resultate dieser Titrationen, zusammen mit den nötigen Angaben für die Durchführung der Titrationen sind in Tabelle I zusammengefasst. 1 ml 0.1 *N* Pb(IV)-Azetat entspricht 10.2195 mg Tl.

Für die Bestimmung von kleinen Thalliummengen war es bereits nötig, die Chlorwasserstoffsäure p.a. zu reinigen. Dabei erhielten wir eine ungefähr 5.5 *N* Chlorwasserstoffsäure, mit der wir die Azidität der titrierten Lösungen einstellten, so dass wir die eigentlichen Titrationen in höchstens 5.1 *N* HCl-Lösungen durchführen konnten. Wir haben gefunden, dass es in einem Anfangsvolumen von 35 ml, unter Verwendung von 0.01 *N* Pb(IV)-Azetat möglich ist, in einem Medium von 4.3–5.1 *N* HCl sehr

TABELLE II

TITRATION VON Tl(I) MIT 0.01 *N* PbAc$_4$ IN EINEM MEDIUM VON 4.3–5.1 *N* HCl

(0.511–8.175 mg Tl; Volumen = 35 ml)

| *Gegeben (mg)* | *Gefunden (mg)* | *Abweichung (%)* | *Potenzialänderung in Equivalenzpunkt* | *Inflexions potenzial* | *Konzentration HCl (N)* |
|---|---|---|---|---|---|
| 0.511 | 0.512 | +0.20 | 180[a] | 710 | 5.1 |
| 0.511 | 0.510 | −0.20 | 160[a] | 710 | 5.1 |
| 1.022 | 1.019 | −0.29 | 200[a] | 730 | 4.7 |
| 1.022 | 1.024 | +0.20 | 170[a] | 710 | 4.7 |
| 1.022 | 1.020 | −0.20 | 150[a] | 720 | 4.7 |
| 2.555 | 2.552 | −0.12 | 180[b] | 700 | 5.1 |
| 2.555 | 2.548 | −0.27 | 170[b] | 680 | 5.1 |
| 2.555 | 2.554 | −0.04 | 180[b] | 690 | 5.1 |
| 5.110 | 5.108 | −0.04 | 190[b] | 705 | 4.7 |
| 5.110 | 5.106 | −0.08 | 200[b] | 710 | 4.7 |
| 5.110 | 5.109 | −0.02 | 195[b] | 715 | 4.7 |
| 8.175 | 8.165 | −0.11 | 210[b] | 710 | 4.3 |

[a] Für 0.005 ml Massreagens
[b] Für 0.01 ml Massreagens

genau 0.51–8.17 mg Tl zu bestimmen. Zum Unterschied von der Bestimmung höherer Thalliummengen wurde Tl(I)-Chlorid nicht ausgeschieden, das Potenzial stellte sich im ganzen Verlauf der Titration sofort ein, die Potenzialänderung in der Equivalenz war gross. Die Resultate der Bestimmung sind sehr genau (siehe Tabelle II). Da die Verbindungen des einwertigen Thalliums in definiertem Zustande leicht erhältlich sind, und ihre Lösungen sehr beständig sind, ist die angeführte Methode zur Bestimmung des Faktors von 0.01 *N* Pb(IV)-Azetat Lösungen, die bei Mikrotitrationen verwendet werden, geeignet.

### *Mikrobestimmung von Thallium*

Da auch bei Anwendung von 0.01 *N* Pb(IV)-Azetat Lösungen der Verlauf der Titrationen sehr befriedigend war, und die Resultate sehr genau waren, versuchten wir auch Thallium in Mikrogrammengen zu bestimmen.

Lösungen, die 10–511 $\mu$g Tl enthielten, haben wir mit gereinigter Chlorwasserstoffsäure (5.5 *N*) so angesäuert, dass in einem Volumen von 35 ml die HCl-Konzentration 4.1 bis 4.7 *N* war. Bei der Titration haben wir aus der Mikrobürette zuerst grössere Mengen des Reagens zugegeben, bei nähernder Equivalenz haben wir den Titrationsschritt stetig herabgesetzt, bis herunter zu 0.001 ml (im Falle von 255 $\mu$g Tl) bzw. 0.0005 ml (im Falle von 10 $\mu$g Tl). In der Nähe des Equivalenzpunktes warteten wir auf die Einstellung des Potenzials höchstens 15 Sek, vorauf wir sofort einen weiteren Anteil des Reagens zugaben (besonders bei der Titration von 10 $\mu$g Tl). 0.001 ml 0.01 *N* Pb(IV)-Azetat entspricht 1.02195 $\mu$g Tl. Bei der Mikrotitration wirken reduzierende Stoffe, die selbst in der gereinigten Chlorwasserstoffsäure anwesend sind, störend. Es muss desshalb ein Blindversuch durchgeführt werden, bei dem mit Pb(IV)-Azetat bis zum Potenzialwert des Equivalenzpunktes der eigentlichen Titration titriert wird. Das ermittelte Reagensvolumen wird von dem Verbrauch bei der eigenen Titration abgezogen. Die Resultate der Thallium-Mikrobestimmung sind in Tabelle III angegeben.

TABELLE III

MIKROTITRATION VON EINWERTIGEM THALLIUM MIT 0.01 *N* $PbAc_4$ IN EINEM MEDIUM VON 4.1–4.7 *N* HCl
(Volumen = 35 ml)

| | *Verbrauch 0.01 N* $PbAc_4$ | | | | | |
|---|---|---|---|---|---|---|
| *Gegeben* (*$\mu$g*) | *bei der eigentlichen Titration* (*ml*) | *bei dem Blindversuch* (*ml*) | *Differenz die der oxydation von Tl entspricht* (*ml*) | *Gefunden* (*$\mu$g*) | *Abweichung* (*%*) | *Potenzialänderung im Equivalenzpunkt* |
| 510.97 | 0.5035 | 0.0030 | 0.5005 | 511.48 | +0.10 | 50[a] |
| 255.49 | 0.2529 | 0.0030 | 0.2499 | 255.38 | —0.04 | 70[a] |
| 127.74 | 0.1270 | 0.0032 | 0.1238 | 126.52 | —0.95 | 30[b] |
| 51.10 | 0.0530 | 0.0032 | 0.0498 | 50.89 | —0.41 | 20[b] |
| 51.10 | 0.0535 | 0.0030 | 0.0505 | 51.61 | +1.00 | 30[b] |
| 51.10 | 0.0529 | 0.0028 | 0.0501 | 51.20 | +0.20 | 40[b] |
| 25.55 | 0.0273 | 0.0028 | 0.0245 | 25.04 | —1.99 | 35[b] |
| 10.22 | 0.0137 | 0.0030 | 0.0107 | 10.93 | +6.95 | 20[b] |
| 11.24 | 0.0141 | 0.0032 | 0.0109 | 11.14 | —0.89 | 20[b] |
| 10.22 | 0.0123 | 0.0030 | 0.0093 | 9.50 | —7.04 | 30[b] |

[a] Für 0.001 ml Massreagens
[b] Für 0.0005 ml Massreagens

Aus den in der vorliegenden Arbeit erreichten Resultaten ist zu ersehen, dass die Titration von einwertigem Thallium mit Pb(IV)-Azetat verlässlich, und in ihrer Durchführung einfach ist. Die Methode ist sehr genau, und ihre Empfindlichkeit ist besser als bei allen bisher angewandten massanalytischen Methoden, denn selbst Mengen um 10 $\mu g$ Tl können mit genügender Genauigkeit in genügend grossem Volumen, d.h. in ungefähr $2 \cdot 10^{-6}$ *M* Lösungen, bestimmt werden, unter Verwendung von geläufigen Apparaturen. Die Methode ist weiter ein Beitrag zu den Möglichkeiten der Bestimmung des Faktors von 0.01 *N*, bzw. noch mehr verdünnten Lösungen des Massreagens, sofern reine Substanzen von Thallium(I)-Salzen als Standarde angewandt werden.

## ZUSAMMENFASSUNG

In den, mit Chlorwasserstoffsäure passend angesauerten Lösungen kann das einwertige Thallium durch eine direkte potentiometrische Titration mit einer Masslösung von Blei(IV)-Azetat titriert werden. Unter Anwendung einer Mikrobürette kann noch 10 $\mu g$ Tl in einem Volumen von 35 ml bestimmt werden.

## SUMMARY

Thallium(I) can be determined by direct potentiometric titration with lead tetraacetate solution in hydrochloric acid media. As little as 10 $\mu g$ of thallium in 35 ml of solution can be determined accurately.

## RÉSUMÉ

Les auteurs décrivent une méthode de dosage du thallium(I) par titrage potentiométrique direct, au moyen de tétracétate de plomb, en solution chlorhydrique.

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# DETERMINATION OF AMINES, PYRIDINE AND NICOTINE BY THERMOMETRIC TITRATION

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(Received February 17th, 1961)

The most commonly used methods[1-3] for the determination of amines, pyridine and nicotine are (*a*) Kjeldahl, (*b*) acetylation, (*c*) bromination, (*d*) diazotisation or nitrosation, and (*e*) titration with acids. Method (*a*) is time-consuming; in (*b*) and (*c*) alcohols and phenols interfere and in (*d*) the end-point is hard to detect. The main draw-back of method (*e*) is that it is not applicable to aqueous solutions of amines and pyridine which behave as very weak bases. Potentiometric titration is not useful in aqueous solution because it is difficult to locate the end-point. It has been observed that amines and pyridine, which behave as very weak bases, can be titrated in aqueous solutions by a thermometric method. The present paper describes the determination of six amines, pyridine and nicotine in aqueous solution by thermometric titration with mineral acids and sodium nitrite solution.

## EXPERIMENTAL

### *Apparatus*

The arrangement for thermometric titration has already been described[4].

### *Reagents*

The reagents used were of A.R. quality. The amines, pyridine and nicotine were used only after distillation at their respective boiling points. Solutions of known strength of the compounds under study were prepared by dissolving a known weight of the substance in water and diluting to a definite volume. The strength of each solution was further checked by the known methods mentioned above. The mineral acids were standardized against standard sodium hydroxide, the strength of which was determined by titrating against succinic acid solution with phenolphthalein as an indicator. The sodium nitrite solutions were standardized by titration with standard potassium permanganate solution.

## GENERAL PROCEDURE

The sample solution containing amine, pyridine or nicotine is placed in the inner Dewar flask and is allowed to attain a constant temperature, which is observed with a Beckmann Thermometer. The standard solution of acid or sodium nitrite solution, which is usually 8–10 times stronger than the base titrated, is placed in the waterjacketted burette and is added in small increments (0.5 or 1.0 ml) every 2 min. The change in temperature, which attains a constant value within 2 min of each addition of titrant, is noted. The curves are obtained by plotting the volume of acid or sodium nitrite solution added as abscissa and the total change in temperature, after applying volume correction, as ordinate. The amount of the base is determined from the position of the break in the titration curves.

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The determination of the following compounds has been studied: (*1*) methylamine, (*2*) ethylenediamine, (*3*) diethylamine, (*4*) aniline, (*5*) *o*-toluidine, (*6*) *m*-aminophenol, (*7*) pyridine, and (*8*) nicotine.

Mixtures of (*1*) ethylenediamine and pyridine, (*2*) ethylenediamine and aniline, (*3*) diethylamine and pyridine, (*4*) diethylamine and aniline, (*5*) pyridine and aniline, (*6*) ethylenediamine, pyridine and aniline, and (*7*) diethylamine, pyridine and aniline were also examined.

The total volume of the solution taken for titration was 40 ml except in the titrations of aniline and pyridine with hydrochloric acid in which the volume of the solution titrated was 50 ml.

## RESULTS AND DISCUSSION

In the titration curves of methylamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine with hydrochloric acid, a sharp break was observed at the point corresponding to the addition of one equivalent of acid. The break in the titration curve of ethylenediamine corresponded to the addition of two equivalents of acid. The titration curve of nicotine also indicated a break at this point. Similar titration curves were also obtained with sulphuric and nitric acids. In all cases, the break was found to be independent of the concentrations of the reagents used and was not affected by the presence of ethyl alcohol, isopropyl alcohol and phenol. No break was observed in the titration curve of compounds with water or of water with acids. Comparison of the curves of *o*-toluidine and of aniline suggests that the methyl group in the *ortho* position to the amino group does not influence the sharp break at the equivalent point. On the other hand attempts to determine *o*-nitroaniline by this method were unsuccessful because the temperature change caused by the addition of acid was too small.

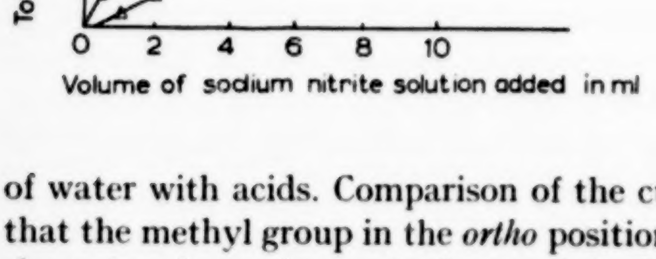

Fig. 1. Curve I: 0.168 *M* HCl and 0.24 *M* $NaNO_2$; Curve II: 0.0125 *M* ethylenediamine + 0.0125 *M* aniline + 0.025 *M* pyridine + excess HCl and 0.240 *M* $NaNO_2$ solution.

When mixtures of ethylenediamine or diethylamine and pyridine or aniline were titrated with hydrochloric acid, two breaks were observed in the titration curves.

The total concentration of the base and that of ethylenediamine or diethylamine were indicated by the second and first breaks respectively. A mixture of pyridine and aniline in aqueous solution was analysed by first titrating with hydrochloric acid and then with sodium nitrite solution. The amount of aniline in the mixture was obtained from the break in the sodium nitrite titration curve. The blank titration of hydrochloric acid with sodium nitrite gave a straight line (Fig. 1, curve I). The two titration methods were also used for the determination of aniline, pyridine and diethylamine or ethylenediamine in a mixture. But the mixture containing ethylenediamine could be successfully titrated only when the titration with sodium nitrite solution was completed within 20 min from the time of first addition of sodium nitrite solution. Otherwise, the rise in temperature after each addition of sodium nitrite solution, did not attain a constant value. A typical thermometric titration curve of a mixture of ethylenediamine, pyridine and aniline (in presence of excess of hydrochloric acid) with sodium nitrite is shown in Fig. 1 (curve II). The results of the thermometric titrations are summarized in Tables I and II.

TABLE I

(p$K_a$ represents the acid dissociation constant of the base)

| *Compound* | *p$K_a$*[5] | *Amount of substance per 40 ml (mg)* | | *Error (%)* |
|---|---|---|---|---|
| | | *Present* | *Found* | |
| methylamine | 10.6 | 51.3 | 51.0 | —0.6 |
| | | 34.1 | 34.4 | +0.9 |
| | | 17.1 | 17.2 | +0.6 |
| ethylenediamine | 7.5 (p$K_a$ 1)<br>10.2 (p$K_a$ 2) | 93.9 | 93.8 | —0.1 |
| | | 45.7 | 45.6 | —0.2 |
| | | 11.4 | 11.3 | —0.9 |
| diethylamine | 11.0 | 70.5 | 70.6 | +0.1 |
| | | 33.4 | 33.2 | —0.6 |
| | | 16.6 | 16.8 | +1.2 |
| aniline | 4.6 | 186.2 | 187.2 | +0.5 |
| | | 93.1 | 93.6 | +0.5 |
| | | 46.0 | 45.6 | —0.9 |
| *o*-toluidine | 4.4 | 110.9 | 112.0 | +1.0 |
| | | 53.2 | 53.6 | +0.8 |
| *m*-aminophenol | — | 244.8 | 245.6 | +0.3 |
| | | 61.2 | 61.6 | +0.7 |
| pyridine | 5.2 | 158.0 | 159.0 | +0.6 |
| | | 79.1 | 79.5 | +0.5 |
| | | 39.5 | 39.7 | +0.5 |
| nicotine | 3.15[a] (p$K_a$ 1)<br>7.85 (p$K_a$ 2) | 243.2 | 245.6 | +1.0 |
| | | 162.2 | 162.5 | +0.2 |
| | | 81.0 | 81.2 | +0.2 |

[a] Calculated from the published data.

It is observed from the results reported in Table I that nicotine, pyridine and the amines studied can be determined by this method with an accuracy better than 1.3% within the concentration range used. The results in Table II indicate that mixtures of aniline, pyridine and diethylamine or ethylenediamine in aqueous solution can be analysed with an accuracy of ± 1.5%. The main advantages of this method are that amines, pyridine and nicotine and their mixtures can be determined in dilute aqueous solutions and that the method is free from the interfering effects of alcohols and phenol.

TABLE II

| *Mixture No.* | *Compounds* | *Amount of substance per 40 ml (mg)* | | *Error (%)* |
|---|---|---|---|---|
| | | *Present* | *Found* | |
| 1 | ethylenediamine | 59.2 | 59.2 | 0.0 |
| | pyridine | 79.2 | 78.8 | —0.5 |
| 2 | ethylenediamine | 59.2 | 59.2 | 0.0 |
| | aniline | 93.2 | 92.8 | —0.4 |
| 3 | diethylamine | 69.6 | 69.2 | —0.6 |
| | pyridine | 59.2 | 59.6 | +0.7 |
| 4 | diethylamine | 69.6 | 69.2 | —0.6 |
| | aniline | 70.0 | 70.4 | +0.7 |
| 5 | aniline | 93.2 | 92.0 | —1.3 |
| | pyridine | 39.6 | 39.8 | +0.5 |
| 6 | diethylamine | 62.0 | 62.4 | +0.7 |
| | aniline | 46.4 | 46.0 | —0.9 |
| | pyridine | 79.2 | 79.6 | +0.5 |
| 7 | ethylenediamine | 39.0 | 39.4 | +1.0 |
| | aniline | 46.4 | 46.8 | +0.9 |
| | pyridine | 79.2 | 78.0 | —1.5 |

## ACKNOWLEDGEMENT

Our thanks are due to the Ministry of Scientific Research and Cultural Affairs, Government of India, for awarding a Senior Research Scholarship to one of us (R. D. Daftary).

## SUMMARY

Thermometric titrations with acids and sodium nitrite solution are described for the determination of methylamine, ethylenediamine, diethylamine, aniline, *o*-toluidine, *m*-aminophenol, pyridine and nicotine. The method is applicable to dilute aqueous solutions; alcohols and phenol do not interfere. Mixtures of aniline, pyridine and diethylamine or ethylenediamine can be analysed. The accuracy of the method is ± 1.5%.

## RÉSUMÉ

Une méthode est proposée pour le dosage des amines, de la pyridine et de la nicotine par titrage thermométrique. Des mélanges d'aniline, de pyridine et de diéthylamine (ou d'éthylènediamine) ont pu ainsi être analysés.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Aminen, Pyridin und Nikotin durch thermometrische Titration. Das Verfahren eignet sich auch zur Analyse von Basengemischen. Alkohole und Phenol stören nicht.

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# NOUVELLE MÉTHODE DE DOSAGE DE TRACES DE CARBONE APPLICATION AU SILICIUM ET AU GERMANIUM

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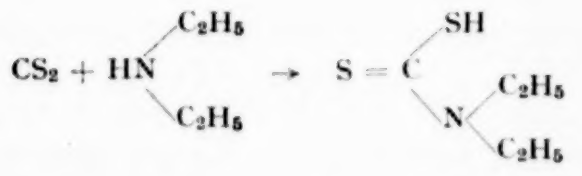
(Reçu le 20 avril, 1961)

La sensibilité de la méthode classique qui utilise le dosage de l'anhydride carbonique formé après oxydation de la matière à analyser, paraissait insuffisante pour la détermination des traces de carbone dans les matériaux semi-conducteurs qui sont à priori de haute pureté. En substituant le soufre à l'oxygène, nous avons mis au point une méthode d'une plus grande sensibilité dont le principe est le suivant: si par réaction avec de la vapeur de soufre à pression et température convenablement choisies la matière à analyser se transforme en sulfures, il est probable que parallèlement les traces de carbone donnent quantitativement du sulfure de carbone puisque ces deux éléments se combinent facilement. Le dosage de ce corps qui peut être recueilli par dissolution dans un solvant organique a fait l'objet de plusieurs publications et sa détermination à l'état de traces dans divers solvants est devenue classique; la limite de sensibilité étant de l'ordre de 1 p.p.m.

Nous proposons le schéma opératoire général suivant: la matière à analyser pulvérulente ou non est placée avec un léger excès de soufre pur, sous vide, dans un tube de verre ou de quartz. Le tube est porté à une température convenable pour que se forment les sulfures des principaux constituants de la matière à analyser ainsi que le sulfure de carbone. Après refroidissement, une extrémité du tube est brisée dans un solvant organique comme le benzène qui monte dans le tube et dissout les traces de sulfure de carbone. Le dosage de ce composé est ensuite effectué après transformation en acide diéthyldithiocarbamique par action de la diéthylamine suivant la réaction:



Avec certains cations métalliques comme l'ion cuivrique, cet acide donne des sels colorés solubles dans le benzène qui sont dosés par colorimétrie.

## APPLICATION AU SILICIUM

Gabriel et Alvarez-Tostado[1] ont montré que le soufre et le silicium se combinent directement mais parfois difficilement. La réaction:

$$Si + S_2 \rightarrow SiS_2 + 59.9 \text{ Kcal}$$

a lieu à haute température et doit être catalysée par de la laine de verre.

Nous avons constaté que cette combinaison se forme en présence de laine de quartz au-dessus de 1000°, la pression de vapeur du soufre (diatomique à cette température) dans les tubes à réaction atteignant plusieurs atmosphères par cm$^2$.

Ces conditions opératoires sont très favorables à la formation du sulfure de carbone. On sait que ces deux éléments se combinent facilement dans un assez vaste domaine de température dont on peut fixer grossièrement les frontières à 600° et 1300°. La température et la vitesse de formation dépendent essentiellement de l'état physique du carbone et de la pression de vapeur du soufre comme l'ont montré par exemple les travaux de MARKOVSKII[2], STULL[3], TROTTER[4], ainsi que l'étude cinétique de formation de GUÉRIN ET ADAM-GIRONNE[5,6].

### *Mode opératoire*

Certaines précautions doivent être prises afin d'éviter l'apport de traces de carbone par les poussières atmosphériques ou par diverses manipulations des tubes à réactions.

#### *Préparation des échantillons*

Avant broyage, le silicium à analyser, le mortier et son pilon, le tamis, les spatules sont lavés avec un solvant chloré comme le dichloréthane, puis à l'alcool pur et rincés à l'eau bidistillée dans un appareil en quartz. L'ensemble est séché au dessicateur.

#### *Broyage du silicium*

Le silicium est broyé au mortier d'agate dans une boîte à gants sans ventilation, puis tamisé (Tamis 19 AFNOR).

#### *Préparation du soufre pur*

Il est préparé par addition d'un excès d'acide chlorhydrique pur (Prolabo R.P.) à une solution de thiosulfate de sodium ($Na_2S_2O_3 \cdot 5\ H_2O$, Prolabo R.P.). Le soufre est filtré sur un creuset en verre fritté No. 4, rincé à l'eau bidistillée et séché au dessicateur.

#### *Préparation des tubes de quartz*

Les tubes de quartz (fabriqués le plus souvent par étirage dans une filière en graphite) sont préalablement chauffés dans un four pendant 1 h à 800° dans un courant d'oxygène. La laine de quartz utilisée dans ce mode opératoire subit le même traitement. Les dimensions initiales d'un tube à réaction sont les suivantes: longueur 15 cm, diamètre intérieur 0.7 cm, diamètre extérieur 0.9 cm. On forme par soufflage à une extrémité un "col de cygne" dont la pointe est laissée ouverte. À l'autre extrémité est soudé un rodage RIN No. 1. Après ces manipulations le tube est de nouveau chauffé pendant 15 min à 800° dans un courant d'oxygène. Après refroidissement, le tube est fermé à sa sortie du four par un tampon de laine de quartz, puis la pointe du "col de cygne" est scellée au chalumeau.

#### *Remplissage des tubes*

Un tampon de laine de quartz est introduit à l'aide d'un agitateur au fond de chaque tube; le silicium pulvérulent et le soufre sont ajoutés et placés au contact de la laine.

L'expérience ayant montré que le silicium "pur" renferme souvent plus de 500 p.p.m. de carbone, la prise d'essai doit être faible.

Pour chaque analyse nous effectuons 3 dosages avec des masses croissantes de silicium (5, 10, 15 mg) et une masse constante de soufre pur en excès (45 mg). Chaque tube est ensuite séparé du rodage et scellé sous un vide d'environ $10^{-2}$ mm de mercure. Après cette opération, la longueur totale du tube est voisine de 10 cm.

### *Chauffage des tubes*

Les tubes sont portés au four entre 1000° et 1100° pendant 1 h. Si la réaction a eu lieu, les produits forment des paillettes blanches de sulfure de silicium.

### *Dosage du sulfure de carbone formé*

Après refroidissement le "col de cygne" est brisé dans un petit bécher en polyéthylène renfermant 4 ml de benzène (Prolabo R.P.). Le liquide monte presque jusqu'en haut du tube qui est ensuite légèrement incliné pour que toute la paroi interne soit au contact du benzène. La deuxième extrémité du tube est cassée à l'aide d'une pince; le benzène est versé dans une ampoule à décanter. Le tube et le bécher sont rincés avec 2 ml de benzène qui sont versés dans l'ampoule. Le tout est agité pendant 1 min avec 5 ml d'une solution de soude environ normale dans le but d'éliminer les traces d'hydrogène sulfuré, produit de l'hydrolyse du sulfure de silicium par les traces d'eau du solvant et l'humidité atmosphérique. Le benzène est ensuite agité pendant 1 min avec 5 ml d'eau bidistillée. Nous avons vérifié que ces opérations n'éliminent aucune trace de sulfure de carbone. Après avoir ajouté 5 gouttes de diéthylamine à la solution benzénique, celle-ci est agitée durant 1 min avec 5 ml d'une solution aqueuse de sulfate de cuivre à 1%. On laisse décanter 15 min à l'abri de la lumière, sépare la couche organique et l'amène exactement à 10 ml. Si sa densité optique est trop élevée, on en prélève 1 ml que l'on dilue exactement 5 fois par exemple.

La colorimétrie est effectuée sur un appareil Jean-Constant à 435 m$\mu$ dans une cuve de 1 cm. Un essai à blanc est effectué dans les mêmes conditions sur le benzène pur.

### *Étalonnage*

Une solution titrée de sulfure de carbone dans le benzène (1 g/l environ) est préparée par pesée dans une fiole jaugée. Par dilution exacte, cette solution permet de tracer la courbe d'étalonnage.

### *Résultats expérimentaux*

(*1*) Un essai effectué en ne mettant que du soufre pur dans un tube à réaction a donné un résultat nul.

(*2*) Dans le Tableau I sont rassemblés les résultats de deux analyses. La teneur en carbone de divers échantillons de silicium (pour semi-conducteurs) que nous avons analysés est comprise entre 500 et 2000 p.p.m.

(*3*) La vérification de cette méthode d'analyse a été effectuée de la façon suivante: l'analyse d'un lot de silicium a révélé la présence de 1700 ± 50 p.p.m. de carbone. Ce lot de silicium a servi au tirage d'un cristal de 20 g dopé par addition de carbure de silicium de manière que sa teneur en carbone augmente de 1000 p.p.m. Tout le cristal a été broyé, tamisé et homogénéisé. Une nouvelle analyse a montré une teneur en carbone de 2700 ± 70 p.p.m.

TABLEAU I

| | *Prises d'essais (mg)* | *Densité optique* | *Teneur en carbone (p.p.m.)* |
|---|---|---|---|
| | | *Avec dilution* | |
| | 5 | 0.063 | 1355 |
| Silicium A | 10 | 0.120 | 1290 |
| | 15 | 0.185 | 1330 |
| | | *Sans dilution* | |
| | 5 | 0.210 | 903 |
| Silicium B | 10 | 0.395 | 850 |
| | 15 | 0.605 | 866 |

## APPLICATION AU GERMANIUM

Le mode opératoire précédent s'applique. Toutefois le germanium renfermant moins de carbone que le silicium, la prise d'essai doit être plus importante (150 mg par exemple). De plus le volume total de benzène utilisé pour la récupération des traces de sulfure de carbone peut être limité à 5 ml.

La teneur des divers échantillons que nous avons analysés est comprise entre 5 et 10 p.p.m.

## RÉSUMÉ

La méthode utilise la formation de sulfure par action de la vapeur de soufre (en tube scellé) sur la matière à analyser portée à une température déterminée. Parallèlement les traces de carbone donnent du sulfure de carbone qui est dosé après dissolution dans un solvant organique. Dans le cas du silicium le schéma opératoire est le suivant: on place dans un petit tube de quartz un mélange de silicium pulvérisé et de soufre pur préparé par voie chimique. L'une des extrémités du tube présente la forme d'un "col de cygne" facile à briser. Le tube est scellé sous vide, puis porté durant une heure entre 1000 et 1100°. Après refroidissement, le "col de cygne" est brisé dans un récipient renfermant du benzène. Le solvant monte dans le tube et dissout le sulfure de carbone. Après addition de diéthylamine, on effectue la colorimétrie du diéthyldithiocarbamate formé. Les résultats obtenus montrent que la teneur en carbone du silicium "pour semi-conducteur" est élevée; elle varie entre 500 et 2000 p.p.m. Le germanium par contre ne renferme que quelques p.p.m. de carbone.

## SUMMARY

A new method is proposed for the determination of traces of carbon in silicon and germanium. The sample is converted to the sulphide by treatment with sulphur vapour in a sealed tube at 1000–1100°. Carbon thus forms carbon disulphide which is determined colorimetrically as diethyldithiocarbamate after dissolution in an organic solvent and addition of diethylamine. Results show that silicon "for semi-conductors" contains 500–2000 p.p.m. of carbon. However, germanium contains only a few p.p.m. of carbon.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Kohlenstoff in Silizium und Germanium durch Überführung in die Sulfide. Der dabei gebildete Schwefelkohlenstoff wird in der Form von Diäthyldithiocarbamat colorimetrisch bestimmt.

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# DIE ANALYTISCHE ANWENDUNG DER KOHLENDIOXYDDESTILLATION

## I. BESTIMMUNG VON AMEISENSÄURE (FORMIAT) ÜBER DAS BEI DER OXYDATION MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD

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(Eingegangen den 15. April, 1961)

Zur Bestimmung der Ameisensäure werden im allgemeinen oxydimetrische Methoden verwendet. Durch verschiedene Oxydationsmittel — wie Kaliumpermanganat, Brom, Jodsäure oder Kaliumbichromat — wird die Ameisensäure zu Kohlendioxyd oxydiert. Die verschiedenen Autoren bestimmen den Überschuss des Oxydationsmittels jodometrisch. Diese Reaktionen sind wenig selektiv und zur Durchführung von Bestimmungen in Gegenwart anderer Reduktionsmittel nicht geeignet.

Mit Quecksilber(II)chlorid reagiert die Ameisensäure unter Bildung von Kohlendioxyd und Quecksilber(I)chlorid.

$$HCOOH + 2\,HgCl_2 = Hg_2Cl_2 + 2\,HCl + CO_2$$

Wenn die gebildete Salzsäure gebunden wird, so verläuft die Reaktion quantitativ und kann auch analytisch verwertet werden. Mit der analytischen Verwendung dieser Reaktion beschäftigten sich bereits mehrere Autoren. FINCKE[1] bestimmte das im Laufe der Reduktion gebildete Quecksilber(I)chlorid gravimetrisch. Auch SZELÉNYI[2] sowie AUERBACH UND ZEGLIN[3] bauten ihre Verfahren auf die Bestimmung des Quecksilber(I)chlorids auf. Die in der Reaktion gebildete Salzsäure wurde dabei mit Natriumazetat gebunden.

Die gravimetrische Bestimmung ist zwar genau, jedoch langwierig. Die genannten Autoren stellen das Reaktionsgemisch für 3–4 Stunden auf ein Wasserbad. Bei dieser Temperatur verläuft die Reaktion langsam.

Es schien uns zweckmässig, das im Laufe der Reaktion gebildete Kohlendioxyd zu bestimmen; bei Siedetemperatur geht die Umsetzung nämlich rasch vor sich. Die Bestimmung über die Messung des Kohlendioxyds bietet also Vorteile, zumal da sie die selektive Bestimmung der Formiate ermöglicht. Stoffe, die das Quecksilber(II)-chlorid reduzieren, jedoch keine Kohlensäure bilden, stören das Verfahren nicht.

In einer früheren Arbeit[4] beschrieben wir ein einfaches Verfahren zur Bestimmung des Kohlendioxyds. Das $CO_2$ kann ohne Verluste abdestilliert werden, wenn man dafür sorgt, dass keine Kohlensäure-Blasen die als Vorlage verwendete Bariumhydroxydlösung passieren. Die störende Wirkung des Kohlendioxydgehalts der Luft kann durch überschichten der Bariumhydroxydlösung mit Pentan ausgeschaltet werden.

Da die Reaktion zwischen Quecksilber(II)chlorid und Ameisensäure stark pH-abhängig ist, muss für die Bindung der gebildeten Säure gesorgt werden. Um das eventuelle Überdestillieren der Essigsäure zu vermeiden, wurde an Stelle des in der Literatur vorgeschlagenen Natriumazetats Kaliumzitrat als Puffer verwendet. Das Reaktionsgemisch wurde in überschüssiger Menge mit Kaliumchlorid versetzt, dass das Quecksilber(II)chlorid in einen Komplex überführt und so seine Hydrolyse verhindert. Bei der Destillation des Kohlendioxyds muss die Lösung intensiv gekocht werden. Die Anwendung geringer Volumina — die im Laufe des Prozesses konstant gehalten werden — wirkt sich vom Gesichtspunkte der Reaktion günstig aus.

Die Destillation wurde in einem modifizierten SCHULEKschen Mikro-Destillationsapparat durchgeführt (siehe Abb. 1). Vor Beginn der Destillation wird im Siedekolben das entsprechende Reagens gekocht, bis durch das Ausflussrohr des Kühlers 1–2 Min hindurch ein lebhafter Wasserdampfstrom austritt. Der Dampfraum im Apparat wird hierdurch von seinem Luft- und Kohlendioxydgehalt befreit. Durch entsprechende Regelung des Kühlwassers sorgt man nun dafür, dass die Bariumhydroxydlösung im Kühlerrohr bis zu einem gewissen Niveau aufwärts steigt. Zur Sicherung einer kohlendioxydarmen Atmosphäre in der Umgebung des Apparats wird der Kolben mit einem regelbaren elektrischen Heizkörper beheizt.

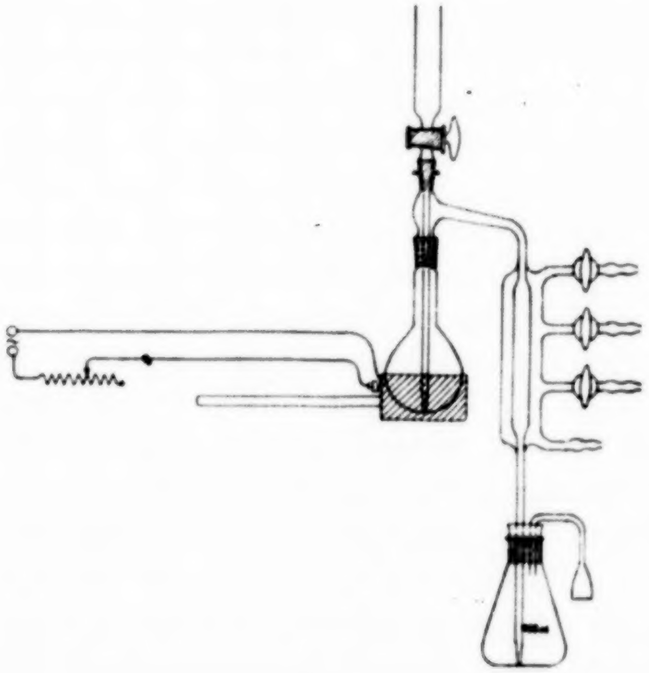

Fig. 1.

Die Reaktion verläuft innerhalb von 20–30 Min quantitativ; während dieser Zeit wird das freigewordene Kohlendioxyd in der als Vorlage verwendeten Bariumhydroxydlösung absorbiert. Der Überschuss des Bariumhydroxyds wird in Gegenwart von Thymolblau-Indikator mit 0.1 bzw. 0.01 *N* Salzsäure zurücktitriert. Bei Bestimmungen im 0.01 *N* Massstabe muss auch eine blinde Destillation bzw. Titration durchgeführt werden. Da das Ergebnis der Titration im 0.01 *N* Massstabe durch das Volumen der Lösung beeinflusst wird, werden die zu titrierenden Lösungen mit ausgekochtem destilliertem Wasser auf ein bestimmtes Volumen (50 ml) ergänzt.

## BESCHREIBUNG DES VERFAHRENS

### *Reagenzien*

10% Quecksilber(II)chlorid, 20% Kaliumchlorid und 25% Kaliumzitrat enthaltende Lösung, 0.1 *N* Bariumhydroxydlösung (enthält 5% Bariumchlorid), 0.01 *N* Bariumhydroxydlösung (enthält 5% Bariumchlorid und 30% Äthanol), 0.1 bzw. 0.01 *N* Salzsäure, 0.3%ige alkoholische Thymolblaulösung, Pentan, Bimsstein ($\phi$ = 1.5–2.0 mm).

### *Verfahren*

Aus der zu untersuchenden Substanz wird mit ausgekochtem destilliertem Wasser eine Stammlösung hergestellt. In den Hahntrichter des Destillationsapparats wird von unten ausgekochtes destilliertes Wasser blasenfrei aufgesaugt und der Hahn dann verschlossen. Der 50-ml fassende Destillationskolben wird beim 20 ml entsprechenden Volumen markiert und dann mit 10 ml Quecksilber(II)chloridlösung beschickt. Nach Zugabe von 10–15 Körnern Bimsstein stellt man den Apparat zusammen und schaltet die Heizung ein. Mit entsprechender Regelung des Schiebewiderstandes wird die Lösung in lebhaftem Sieden gehalten. Nachdem 1–2 Min hindurch Wasserdampf aus dem Kühlerrohr ausgetreten ist, wird der untere Hahn des Kühlers geöffnet, die beiden oberen Hähne werden verschlossen, und das Kühlwasser eingeschaltet. In einen 100-ml Erlenmeyer-Schliffkolben werden 5 ml Pentan gegossen; (beim Arbeiten im 0.01 *N* Massstabe wird das 50 ml entsprechende Volumen am Kolben markiert) dann lässt man aus einer automatischen Bürette 15.00 ml Bariumhydroxydlösung (die unter Pentan steht) in den Kolben einlaufen. Die an der Kolbenwand haftende Bariumhydroxydlösung wird mit einigen ml ausgekochtem destilliertem Wasser unter die Pentanschicht gespült, der Kolben mit Hilfe eines doppelt durchbohrten Korken am Ausflussrohr des Kühlers befestigt und durch die zweite Bohrung im Korken eine Trockenröhre geschoben, in der ein mit Bariumhydroxydlösung durchtränkter Wattebausch untergebracht ist. Das Ausflussrohr des Kühlers muss mit mässigem Druck am Boden des Kolbens anliegen. Der mittlere Hahn des Kühlers wird nun geöffnet und der untere verschlossen; die Bariumhydroxydlösung steigt dann bis zum unteren Drittel des Kühlerrohres auf. Das Niveau der Bariumhydroxydlösung wird während der Destillation bei dieser Höhe gehalten, was durch entsprechendes Schliessen und Öffnen der Hähne erreicht werden kann. Sollte die Absorptionslösung bis unter das untere Drittel des Kühlerrohres absinken, so wird die dritte Kühlungsstufe eingeschaltet.

10.00 ml der zu untersuchenden Lösung werden in den Hahntrichter pipettiert und in kleinen Portionen (zu 0.3–0.5 ml) in den Destillationskolben einlaufen gelassen. Der Hahntrichter wird gleichfalls in kleinen Portionen mit 2 × 5 ml Wasser nachgespült. Man setzt das intensive Sieden 25–30 Min hindurch fort, das abdestillierte Wasser wird dabei nötigenfalls ersetzt. Nach 30 Min wird der untere Hahn des Kühlers geöffnet und der Vorlagekolben soweit gesenkt, dass die Öffnung des Ausflussrohres über der Oberfläche des Pentans zu stehen kommt. Nach 1–2 Min wird das Sieden eingestellt. Beim Arbeiten im 0.01 *N* Massstabe wird das Lösungsvolumen in Vorlagekolben mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Man führt die Titration langsam und unter intensivem Rühren durch, bis die Farbe des Thymolblau-Indikators zu verblassen beginnt. Der Kolben wird nun verschlossen und die niederschlaghaltige Lösung intensiv durchgeschüttelt und dieses Verfahren nach Zugabe weiterer Anteile der Masslösung einige Male wiederholt. Den Endpunkt der Titration zeigt das Erscheinen der grünen Farbe des Indikators an.

Zur Ermittlung des Blindwertes werden 15.00 ml 0.1 *N* Bariumhydroxydlösung in Gegenwart von 5 ml Pentan unter gleichen Bedingungen titriert. Die Differenz bei der Titrationen dient als Grundlage der Berechnung. Bei Verwendung von 0.01 *N* Bariumhydroxydlösung muss zur genauen Erfassung des Blindwertes auch die Destillation durchgeführt werden.

1 ml 0.1 *N* HCl entspricht 3.401 mg, 1 ml 0.01 *N* HCl entspricht 0.3401 mg Natriumformiat.

Die Ergebnisse unserer mit dieser Methode durchgeführten Bestimmungen sind in den Tabellen I und II zusammengefasst.

TABELLE I

BESTIMMUNG DES NATRIUMFORMIATS ÜBER DAS BEI DER OXYDATION MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD (0.1 *N*)

| *Einwaage Natriumformiat*[a] *(g/500 ml)* | *Eingemessene Lösung (ml)* | *Verbrauch 0.1 N $Ba(OH)_2$-Lösung (ml)* | | *Gefunden HCOONa* | |
|---|---|---|---|---|---|
| | | *Einzeln* | *Durchschn.* | *(mg)* | *(%)* |
| 1.9753 | 10.04 | 11.32<br>11.30<br>11.30 | 11.31 | 38.4 | 96.6 |
| | 4.99 | 5.64<br>5.60<br>5.64 | 5.62 | 19.0 | 96.5 |
| | 2.00 | 2.24<br>2.23<br>2.25 | 2.24 | 7.58 | 96.4 |

[a] Das verwendete Natriumformiat wurde durch Oxydation mittels Bichromat und jodometrischer Rücktitration des Bichromatüberschusses kontrolliert. Nach dieser Methode ergab sich ein Natriumformiatgehalt von 96.8%.

TABELLE II

BESTIMMUNG DES NATRIUMFORMIATS ÜBER DAS BEI DER OXYDATION MITTELS QUECKSILBER(II)CHLORID GEBILDETE KOHLENDIOXYD (0.01 *N*)

| *Einwaage Natriumformiat*[a] *(g/500 ml)* | *Eingemessene Lösung (ml)* | *Verbrauch 0.01 N $Ba(OH)_2$-Lösung (ml)* | | *Gefunden HCOONa* | |
|---|---|---|---|---|---|
| | | *Einzeln* | *Durchschn.* | *(mg)* | *(%)* |
| 0.2132 | 10.04 | 12.16<br>12.14<br>12.19 | 12.16 | 4.13 | 96.6 |
| | 4.99 | 6.05<br>6.07<br>6.09 | 6.07 | 2.06 | 96.8 |
| | 2.00 | 2.41<br>2.41<br>2.43 | 2.42 | 0.82 | 96.5 |

[a] Gehalt: 96.8% Natriumformiat

## ZUSAMMENFASSUNG

Zur Bestimmung der Ameisensäure (Formiat) ist als selektive Methode die Oxydation mit Quecksilber(II)chlorid am besten geeignet. Da die gravimetrische Bestimmung des im Laufe der Reaktion gebildeten Quecksilber(I)chlorids langwierig ist, wurde eine einfache Destillationsmethode zur Bestimmung des im Laufe der Reaktion gebildeten Kohlendioxyds ausgearbeitet. Die Methode ist zur raschen titrimetrischen Bestimmung des Formiats sowohl in 0.1 wie auch in 0.01 *N* Massstabe geeignet.

## SUMMARY

Formic acid and formates are best determined by selective oxidation with mercury(II) chloride. The gravimetric determination of the mercury(I) chloride formed is tedious, and the authors propose a simple distillation method for determination of the carbon dioxide formed. Rapid titrimetric determination with 0.1 or 0.01 *N* solutions is possible.

## RÉSUMÉ

L'acide formique et les formiates peuvent être dosés par oxydation au moyen de chlorure de mercure(II). Les auteurs proposent ensuite une simple distillation et un titrage de l'anhydride carbonique formé, ce procédé étant plus rapide que le dosage gravimétrique du chlorure de mercure(I).

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# CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF VARIOUS ELEMENTS WITH α-NITROSO-β-NAPHTHOL

## DETERMINATION OF URANIUM IN SEAWATER

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(Received March 17th, 1961)

The isolation of a variety of elements from very dilute solution by co-crystallization with organic reagents has been described[1]. The general method consists of introducing an appropriate organic reagent into the trace element solution and crystallizing it therefrom by some suitable means. If the compound formed between the microcomponent and the organic reagent is more insoluble than the organic reagent, the crystalline phase is enriched with trace element. Depending upon the degree of enrichment, recovery of more or less of the organic reagent affords the complete recovery of the microcomponent.

This paper describes an extension of the study[1] to include the co-crystallization of a number of trace elements from solution with the organic reagent α-nitroso-β-naphthol.

To permit the measurement of trace quantities of the elements studied, radioactive tracers were used. The distribution of several of these elements between the mother liquor and solid phase was determined upon the crystallization of different quantities of the organic reagent from solution. The influence of carrier concentration and of pH were examined, and the recovery over a range of pH was determined under conditions which provided for maximum reagent crystallization at a definite organic reagent concentration. Finally, application of the co-crystallization process with this system was demonstrated by way of the isolation and subsequent determination of uranium in seawater.

## EXPERIMENTAL

### *Reagents and tracers*

α-Nitroso-β-naphthol was dissolved in acetone at a concentration of 10 mg/ml.

Buffer solutions over the pH range 3–7 were made by mixing appropriate quantities of acetic acid and sodium hydroxide. The pH 8–9 buffer consisted of boric acid and sodium hydroxide. These reagents were of analytical grade and their final concentration in test solutions was limited to 0.1 *M*.

The following radioactive tracers were used: $^{22}$Na(I), $^{59}$Fe(III), $^{60}$Co(II), $^{65}$Zn(II), $^{85}$Sr(II), $^{95}$Zr(IV), $^{103,106}$Ru(III), $^{125}$Sb(III), $^{144}$Ce(III), $^{237}$U(VI), $^{237}$Pu(IV). These isotopes were obtained commercially or, as in the case of $^{237}$U and $^{237}$Pu, were formed by the reactions $^{236}\mathrm{U}\,(n,\gamma)^{237}\mathrm{U}$ at the Materials Testing Reactor and $^{235}\mathrm{U}(\alpha, 2n)$-$^{237}$Pu in the University of California 60″ cyclotron. The oxidation state of the radionuclides was known from the method of preparation or determined analytically[2] in the case of $^{237}$Pu.

The purity of the radionuclides was established by decay measurements which were made throughout the course of experiments and by γ-ray pulse height analysis. Some of the tracers contained inert carrier. In such cases the quantity of tracer introduced into the test solution was limited so that the final concentration of the element was below $10^{-8}$ g/ml.

### *Method*

1 ml of a radioactive tracer, 10 ml of buffer, 5 ml of acetone, and 5 ml of α-nitroso-β-naphthol reagent were thoroughly mixed in a beaker. (In the series of experiments in which the distribution of cerium was determined, 10 ml instead of 5 ml of acetone were added). The vessel was heated in a boiling water bath to evaporate acetone from solution. The amount of acetone evaporated was varied between samples to provide for the crystallization of different quantities of organic reagent. After the variable heating period, samples were transferred to an ice-bath and cooled for 15 min. The solid phase was separated from the mother liquor by filtration. The extent of crystallization was measured by radiometric determination of the organic reagent concentration in the liquid phase[3]. The standard deviation was about 2%.

The quantity of tracer carried by the crystals was determined by γ-ray well scintillation counting after dissolution of the crystals in hot nitric acid and dilution to a definite volume. The count rate was compared with a standard tracer solution which was diluted to the same volume. The γ-ray activity of a definite volume of the mother liquor also was determined in those cases in which the quantity of co-crystallized trace element was small. A sufficient number of counts was accumulated so that the counting error was 1% or less.

## RESULTS AND DISCUSSION

The relation of cobalt recovery to pH and to crystallization of different amounts of the organic carrier from solution is shown in Fig. 1. The marked enrichment of the crystallized carrier with radioelement is apparent. Over the pH range studied, crystallization from solution of only 40% of the reagent assures the quantitative recovery of cobalt.

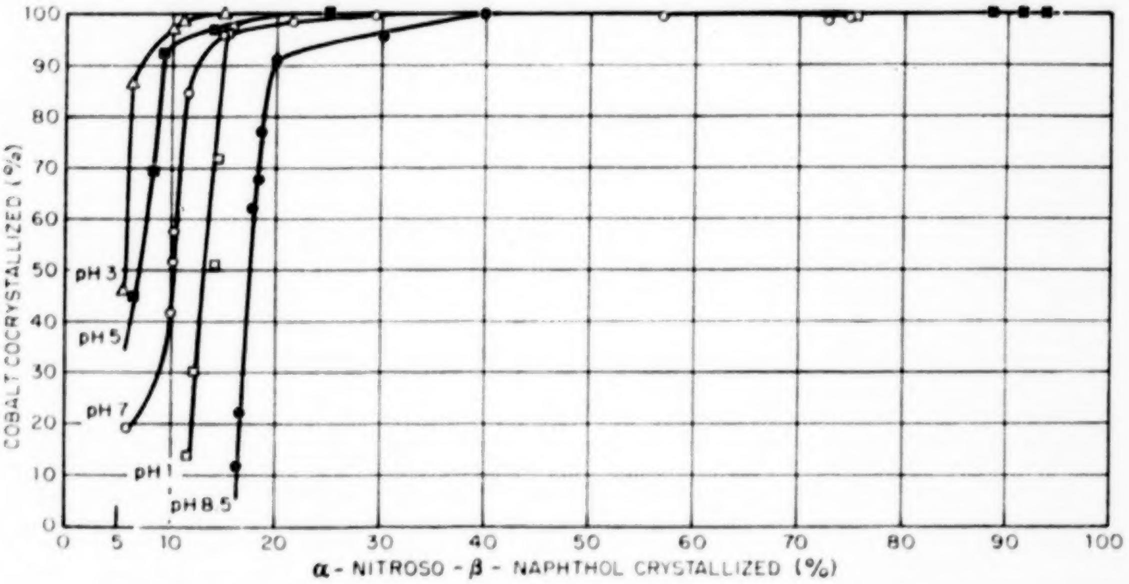

Fig. 1. Co-crystallization of cobalt with α-nitroso-β-naphthol.

The relationship between pH and the recovery of a number of elements upon crystallization of the organic reagent from solution, to the extent afforded by evaporation of samples to their original aqueous volume, appears in Fig. 2. The quantity of organic reagent which crystallized from solution at different hydrogen ion con-

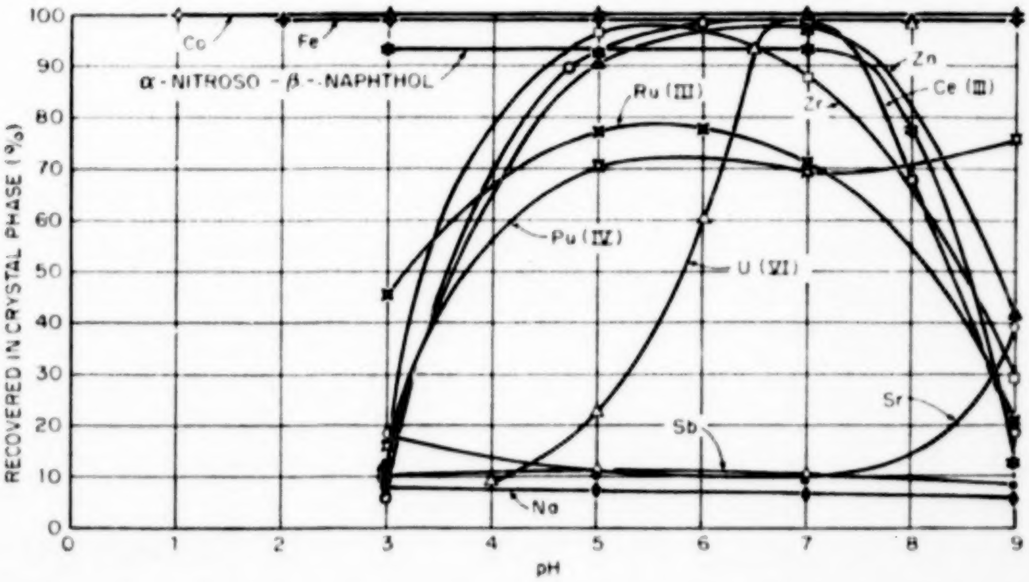

Fig. 2. Influence of pH upon co-crystallization of various elements from solution with α-nitroso-β-naphthol.

centrations is also shown. Cobalt and iron were quantitatively recovered over the entire pH range studied. Cerium and uranium were essentially quantitatively recovered at an optimum pH of 7. Zinc was carried slightly less quantitatively, the maximum recovery also occurring in the region of neutrality. About 97% of zirconium co-crystallized at pH 5, and from 70 to 80% of ruthenium and plutonium were carried in the region pH 5 to 7. Sodium, strontium, and antimony were largely absent from the crystalline phase.

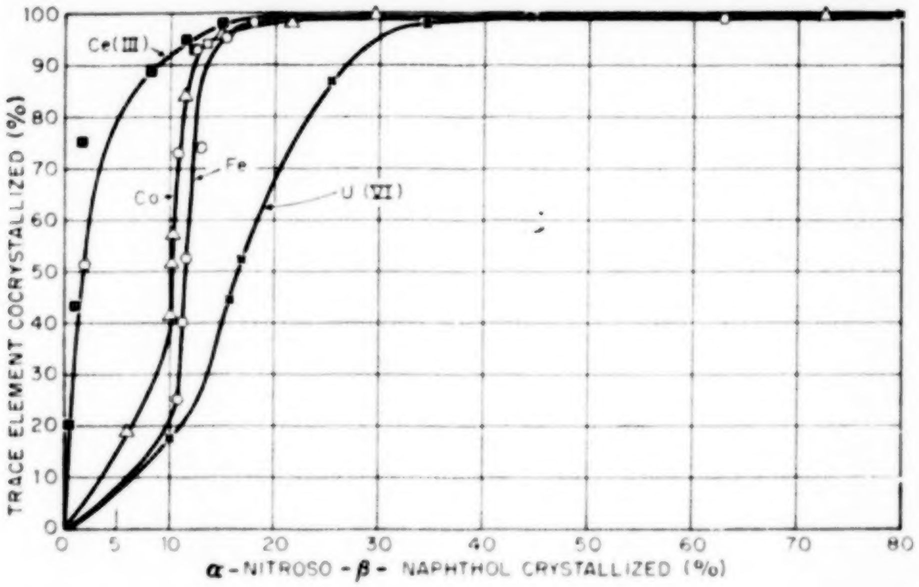

Fig. 3. Co-crystallization of several elements from solution upon crystallization of various fractions of α-nitroso-β-naphthol.

The distribution of cerium, cobalt, iron and uranium between the liquid and solid phases upon crystallization of different quantities of carrier at pH 7 is shown in Fig. 3. Cerium was carried most efficiently, while the other elements co-crystallized in the order cobalt > iron > uranium. With the exception of cerium, which does not form an insoluble naphtholate, this order is consistent with that predicted from Fajans Rule. Each of the naphtholates is more insoluble than the organic precipitant and the greater the insolubility, the greater the degree of enrichment. The solubility of the respective nitroso naphtholates (Table I) was determined by radiometrically measuring the inorganic component in a saturated naphtholate solution. This solution was prepared by stirring the solid compound of known specific activity for 24 h in distilled water at 22.5°.

The method of crystallization was such that the effect of the diffusion of ions

TABLE I

SOLUBILITY IN WATER OF α-NITROSO-β-NAPHTHOL AND SEVERAL NITROSO-NAPHTHOLATES AT 22.5°

| *Compound* | *Solubility (mole/l)* |
|---|---|
| α-Nitroso-β-naphthol | $1.38 \cdot 10^{-3}$ |
| Uranyl-nitroso-naphtholate | $4.50 \cdot 10^{-5}$ |
| Ferric-nitroso-naphtholate | $1.97 \cdot 10^{-5}$ |
| Cobaltic-nitroso-naphtholate | $2.85 \cdot 10^{-6}$ |

within the crystal and of recrystallization was negligible. This type of crystallization normally favors the DOERNER-HOSKINS logarithmic distribution[4] for systems in which the microcomponent is internally incorporated within the crystal. Logarithmic distribution coefficients ($\lambda$) were calculated from the distribution data obtained for cobalt, uranium, and iron (Fig. 3), and are shown in Table II. These values were inconstant and generally increased as the concentration of acetone was reduced and more of the naphthol was crystallized from solution. The varying logarithmic distribution coefficient may be the consequence of the changing acetone concentration, the solubility of the naphtholates being greater in this solvent than in water.

TABLE II

LOGARITHMIC DISTRIBUTION COEFFICIENTS ($\lambda$) FOR THE CO-CRYSTALLIZATION OF COBALT, IRON AND URANIUM WITH $\alpha$-NITROSO-$\beta$-NAPHTHOL

| *Recovered in crystal phase* | | $\lambda^a$ |
|---|---|---|
| *$\alpha$-Nitroso-$\beta$-naphthol (%)* | *Microcomponent (%)* | |
| *Cobalt* | | |
| 6.0 | 18.8 | 3.5 |
| 10.0 | 41.5 | 5.1 |
| 10.2 | 51.6 | 7.0 |
| 10.4 | 57.2 | 7.5 |
| 10.8 | 72.7 | 11.5 |
| 11.5 | 84.0 | 15.0 |
| 15.0 | 95.8 | 19.1 |
| 21.5 | 98.2 | 16.8 |
| *Iron* | | |
| 10.8 | 25.1 | 2.6 |
| 11.3 | 40.0 | 4.2 |
| 11.5 | 52.5 | 6.1 |
| 13.0 | 73.8 | 9.6 |
| 15.4 | 95.4 | 18.6 |
| 18.1 | 98.2 | 20.2 |
| *Uranium* | | |
| 10.0 | 17.5 | 1.8 |
| 15.8 | 44.5 | 3.4 |
| 17.0 | 52.0 | 4.0 |
| 25.5 | 86.8 | 6.9 |
| 34.5 | 98.1 | 9.3 |

[a] $$\log \frac{\text{total tracer}}{\text{tracer in solution}} = \lambda \log \frac{\text{total carrier}}{\text{carrier in solution}}$$

Cerium(III) is carried from solution by a mechanism distinct from that involved in the co-crystallization of those elements which follow Fajans Rule. Examination of aqueous solutions containing macro quantities of cerous salts indicates that the solubility of these salts is markedly reduced by the introduction of acetone in the pH range 5–7. Presumably even in solutions in which the concentration of element is substantially below the solubility product, the inherent propensity for the formation of a solid phase by virtue of the presence of the crystallizing agent is manifested by co-crystallization. Interestingly, when citrate, which inhibits the acetone crystallization of cerous salts from aqueous solution, is added to a solution of cerium(III) tracer and organic carrier, the cerium remains completely associated with the liquid phase after crystallization.

## DETERMINATION OF URANIUM IN SEAWATER

This part of the report describes the application of the co-crystallization of uranium with α-nitroso-β-naphthol in the quantitative analysis of this element in seawater. In the determination of uranium in seawater a preliminary isolation step is required because of the high salt content and the minute uranium concentration. Several methods of separation have been described which depend upon coprecipitation with carriers such as ferric[5] or aluminum hydroxide, iron phosphate[6] and methyl violet thiocyanate[7].

A preliminary experiment was performed to determine the pH and organic reagent concentration required for co-crystallization. Measured quantities of $^{237}$U tracer were added to 50-ml samples of seawater of varying pH and of α-nitroso-β-naphthol concentration. The $^{237}$U recovery is shown in Table III. At a reagent concentration of 8.4 mg/50 ml of seawater and a pH of 7–8, uranium co-crystallized essentially completely. The following procedure was therefore adopted.

TABLE III

INFLUENCE OF pH AND REAGENT CONCENTRATION UPON CO-CRYSTALLIZATION OF URANIUM IN SEAWATER WITH α-NITROSO-β-NAPHTHOL

| α-Nitroso-β-naphthol (mg/50 ml seawater) | pH | Uranium recovered (%) |
|---|---|---|
| 4.2 | 8 | 54.2 |
| 8.4 | 4 | 9.2 |
| 8.4 | 6 | 78.6 |
| 8.4 | 7 | 99.2 |
| 8.4 | 8 | 98.8 |

Surface seawater was collected in a 20-l polyethylene bottle 40 miles due west of San Francisco. The collection was acidified to pH 1 with nitric acid. For yield determination a measured quantity of $^{237}$U tracer was added to two 1-l aliquots of the acidified seawater and the solution was placed on a hot plate for 1 h. After cooling, 20 ml of acetone containing 0.4 g of organic reagent was added and each aliquot was evaporated on a hot plate to about 950 ml and then cooled in an ice bath for 1 h. The crystals which formed were collected on sintered glass by vacuum filtration. The organic residue was dissolved in 20–30 ml of hot concentrated nitric acid, evaporated to near dryness, and wet-ashed with several ml of a 50:50 mixture of concentrated nitric and perchloric acid. The white inorganic residue, weighing about 100 mg, was dissolved in a minimum of water and the solution was made 10 *N* with concentrated hydrochloric acid. This solution was cooled in an ice bath. The crystals which formed were separated by centrifugation and discarded. The supernatant liquid was passed through a bed (7 × 0.62 cm) of Dowex-1 resin (0.297–0.144 mm) previously washed with concentrated hydrochloric acid. The column was then washed with 15 ml of 12 *N* hydrochloric acid and uranium was eluted with 25 ml of 0.5 *N* nitric acid. The eluate was evaporated to dryness. The barely visible residue was dissolved in 10 ml of 0.1 *N* nitric acid. Aluminum nitrate (19 g) was dissolved in this solution with the aid of heat. The uranium was extracted with two 10-ml portions of ethyl acetate to separate it from iron, which interferes with the quantitative analysis. The organic solvent was centrifuged to separate the entrained aqueous phase. The ethyl acetate was carefully decanted into a 25-ml beaker and slowly evaporated to about 3 ml. The solution was transferred to a 5-ml volumetric flask and diluted to volume with ethyl acetate. The $^{237}U$ $\gamma$-ray activity was determined on an aliquot to correct for losses in the chemical yield of uranium. The average recovery at this state of analysis ranged from 80 to 90%. From 0.5 to 1.0 ml of sample was transferred to a small platinum dish and evaporated to dryness. To the dish were added 150 mg of flux of the following composition by weight: 9 parts NaF, 45.5 parts $Na_2CO_3$, 45.5 parts $K_2CO_3$. The quantity of uranium was determined fluorimetrically with a Galvanek-Morrison Fluorimeter (Jarrell-Ash Company, Newtonville, Mass.). The absence of elements which interfere with uranium fluorescence was established through fluorimetric determinations of 0.15–0.94 $\mu g$ quantities of uranium added to 0.5 ml of the seawater–ethyl acetate extract. Three 1-ml aliquots of ethyl acetate were analyzed for each of two seawater samples and the assay was $3.18 \pm 0.06\ \mu g$ of uranium per l of seawater. This value is in close agreement with the value 3.4, recently obtained by independent methods for Atlantic Ocean[8] and Gulf of Mexico[9] waters.

The isolation of uranium from seawater by the co-crystallization process presents several advantages over the usual inorganic carrier co-precipitation techniques. The crystallization is performed simply, relatively rapidly, and the crystals are of such form that they are easily collected. More importantly, uranium is essentially quantitatively separated from the large bulk of the inorganic constituents of seawater in the process. Since the organic reagent is easily removed by wet-ashing and because it carries only a small amount of extraneous salt, the analytical procedure is both simple and reliable.

## SUMMARY

The co-crystallization of ultramicro quantities of various elements with $\alpha$-nitroso-$\beta$-naphthol was investigated. Radiotracer techniques were employed to measure the quantitative removal of these elements from aqueous solutions. Conditions were developed for the separation of cerium(III), zinc, iron(III), cobalt(II), zirconium and uranium(VI) by this process. Plutonium(IV) and ruthenium(III) co-crystallized less completely while sodium, strontium and antimony(III) remained largely associated with the mother liquor. The process was applied in the determination of uranium in seawater. The measured amount was $3.1 \pm 0.1\ \mu g$ uranium/l.

## RÉSUMÉ

Les auteurs ont examiné à l'aide de techniques radiochimiques la co-cristallisation de traces de divers éléments avec l'$\alpha$-nitroso-$\beta$-naphtol. La co-cristallisation de l'uranium a pu être appliquée au dosage de cet élément dans l'eau de mer.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Co-Kristallisation von Ultramikromengen verschiedener Elemente mit $\alpha$-Nitroso-$\beta$-naphthol. Zum Nachweis der quantitativen Entfernung dieser Elemente aus wässriger Lösung wurden radiochemische Methoden benutzt. Das Verfahren eignet sich zur Bestimmung von Uran in Meerwasser.

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# THE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM AND CALCIUM IN PLANT EXTRACTS WITH SPECIAL REFERENCE TO INTERFERENCE EFFECTS

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(Received March 25th, 1961)

In recent years, the flame photometric technique has become very popular, largely because the method is rapid, convenient, simple to use and relatively inexpensive. Moreover the flame photometer is often combined in the same instrument with an absorption spectrophotometer.

DEAN[1] has given a brilliant review of the work which has been carried out in this field. The many published data are, however, often contradictory with regard to the different interference effects and the optimal working conditions. This is partly because the experimental conditions may vary and, partly, because some interference effects have not been investigated.

In working out a flame photometric procedure, the following three points must be considered: (*1*) The optimal working conditions, *i.e.* the optimal parameters with respect to gas pressure, slit width, etc.; (*2*) Interference effects, which may be divided into: (*a*) background effects, (*b*) spectral interference, *i.e.* the overlapping radiations from separate lines of different elements and (*c*) radiation interferences which properly include the effect of an interfering cation or anion, upon the radiation of an analysis element; (*3*) The reproducibility of the method.

A procedure worked out for one type of flame photometer is not directly applicable to another type, even if the principle of the instrument is the same, *e.g.* an instrument with monochromator, photomultiplier and total consumption burner. A procedure which is found to be applicable to one type of flame photometer, *e.g.* Beckman DU, may not be directly applicable to all instruments of this type. Every apparatus has to be tested separately with respect to optimal working conditions (though these will always be found very similar); it is also better to test all the interference effects, and in particular the background, which is largely dependent on the burner setting. Generally, however, only slight adaptations will be necessary.

This paper deals with an investigation made to find a reliable and rapid method for the determination of sodium, potassium and calcium in plant material, with the aid of a Beckman DU spectrophotometer, with flame attachment of the total consumption burner type.

## DETERMINATION OF SODIUM AND POTASSIUM

Studies of flame photometric determinations of sodium and potassium in plant material have been carried out by ATTOE[2], BAUSERMANN[3], BROWN[4,5], JOHNSTON[6], MATHIS[7], MEHLICH[8], OELSCHLAGER[9], PIENAAR[10], PUFFELES[11], SHOJA[12] and their collaborators. All these authors agree that different interference effects may appear in the determination of sodium and potassium in such a complex material as a plant ash extract, but the interferences are not serious and may be compensated for by suitable standard solutions. Any overlapping effect is sufficiently small that filters can be used to isolate the proper radiation, but a monochromator will, of course, give better results.

## *Experimental*

The equipment was adjusted in accordance with the instructions given by the factory. Acetylene–oxygen was selected as a suitable gas mixture. Its high temperature allowed the determination even of very small amounts of the elements in question, and this advantage may compensate for the drawback that the high temperature also causes ionisation, which lowers the intensity of the atomic lines. By proper adjustment of the burner, the background effect could be lowered to a minimum, below a reading of 1.0 on the transmission scale. The oxygen pressure was kept at 10 p.s.i., as is indicated for the proper burner. An acetylene pressure of 3.5–4.0 p.s.i. then gave the highest sensitivity with the lowest background effect. The consumption rate of a 20° solution was 1.6 ml/min. The lines 589 m$\mu$ and 768 m$\mu$ were selected for sodium and potassium respectively, and the other parameters were as follows:

| | *Na* | *K* |
|---|---|---|
| *Slit* | 0.15 mm | 0.1 mm |
| *Sensitivity* | clockwise | midpoint |
| *Selector Switch* | 0.1 | 1.0 |
| *Phototube* | ultraviolet | redsensitive |
| *Load resistance* | 10,000 Me.ohm | 10,000 Me.ohm |

## *Results*

Under these experimental conditions, the interference effects of different ions on the emission intensity of sodium and potassium were tested. The important ions are naturally those occurring in larger amounts; for plant ashes these are sodium, potassium, calcium, magnesium, nitrate, sulphate and phosphate. A systematic study of the interference of each of these ions was carried out by the following procedure.

To two different concentrations of potassium and sodium respectively, three increasing concentrations of the above-mentioned interfering agents were added, and the percentage transmission was read. The metals were added as chlorides, and nitrate, sulphate and phosphate as the respective diluted acids. Readings were taken for the potassium and the sodium concentrations respectively, with and without any addition of interfering materials, and the percentage error introduced by the interfering ions was calculated (Tables I and II).

A blank run on the added elements gave no reading over the background. All readings were replicated. The nitrate, sulphate and phosphate ions caused no interference effects, or at any rate negligible effects.

TABLE I

THE INFLUENCE OF Ca, Mg AND K ON DETERMINATION OF Na

| *Concentration of Na (mg/250 ml)* | *Concentration of added element (mg/250 ml)* | *Reading in % transmission* | *Calculated concentration of Na (mg/250 ml)* | *Error (%)* |
|---|---|---|---|---|
| 2.00 | | 27.5 | 2.00 | |
| 2.00 | Ca 12.5 | 28.1 | 2.08 | 4.0 |
| 2.00 | 25.0 | 28.3 | 2.10 | 5.0 |
| 2.00 | 37.5 | 28.5 | 2.14 | 7.0 |
| 10.00 | | 85.0 | 10.00 | |
| 10.00 | 12.5 | 85.1 | 10.00 | 0.0 |
| 10.00 | 25.0 | 85.9 | 10.20 | 2.0 |
| 10.00 | 37.5 | 86.3 | 10.25 | 2.5 |
| 2.00 | | 28.1 | 2.00 | |
| 2.00 | Mg 4.5 | 28.3 | 2.01 | 0.5 |
| 2.00 | 9.0 | 28.8 | 2.07 | 3.5 |
| 2.00 | 13.5 | 29.1 | 2.10 | 5.0 |
| 10.00 | | 85.3 | 10.00 | |
| 10.00 | 4.5 | 85.8 | 10.20 | 2.0 |
| 10.00 | 9.0 | 86.1 | 10.25 | 2.5 |
| 10.00 | 13.5 | 86.3 | 10.30 | 3.0 |
| 2.00 | | 27.9 | 2.00 | |
| 2.00 | K 40 | 30.3 | 2.26 | 13 |
| 2.00 | 80 | 31.7 | 2.40 | 20 |
| 2.00 | 120 | 32.5 | 2.50 | 25 |
| 10.00 | | 84.5 | 10.0 | |
| 10.00 | 40 | 89.5 | 10.8 | 8 |
| 10.00 | 80 | 92.2 | 11.3 | 13 |
| 10.00 | 120 | 94.5 | 11.7 | 17 |

The metal ions caused a typical enhancement effect, and not overlapping of lines, for the blank gave no effect on the same wavelength.

The effect of potassium particularly on the determination of sodium caused serious analytical errors (Table I). In order to check this strong interference effect, a few herbage samples were analysed and the results calculated from different standard curves, representing the addition of different amounts of potassium (Table III). The Table shows that the error may amount to about 25% and is highest for the low sodium values. As the interference effects are all positive, however, they will be cumulative, hence it is best to compensate for all the interfering elements. This can be achieved in two ways. As appears from Tables I and II, the enhancement effect of the interfering ions does not increase in direct proportion as the amount of ion increases, and if sufficient is added, the curves are often found to flatten out. If a sufficient amount of interfering ions is added both to the sample solutions and to the standards, the interference effect will be compensated. However, relatively large amounts of potassium must be added before the "radiation buffering" zone is reached. The radiation buffer method is the most reliable, but addition of proper amounts of the interfering agents to the standards will also give satisfactory results, and is preferred here.

A sample of 5 g of oven-dried plant material is used for the determination, and this amount contains on average 25 mg Ca, 9 mg Mg, 80 mg K and 3 mg Na. If these

## TABLE II

THE INFLUENCE OF Ca, Mg AND Na ON DETERMINATION OF K

| *Concentration of K (mg/250 ml)* | *Concentration of added element (mg/250 ml)* | *Reading in % transmission* | *Calculated concentration of K (mg/250 ml)* | *Error (%)* |
|---|---|---|---|---|
| 10.00 | | 19.6 | 10.00 | |
| 10.00 | Ca 12.5 | 20.0 | 10.30 | 3.0 |
| 10.00 | 25.0 | 20.2 | 10.45 | 4.5 |
| 10.00 | 37.5 | 20.4 | 10.55 | 5.5 |
| 75.0 | | 89.0 | 75.0 | |
| 75.0 | 12.5 | 89.4 | 75.4 | 0.5 |
| 75.0 | 25.0 | 89.8 | 76.0 | 1.3 |
| 75.0 | 37.5 | 91.0 | 77.3 | 3.1 |
| 10.00 | | 19.1 | 10.00 | |
| 10.00 | Mg 4.5 | 19.1 | 10.00 | 0.0 |
| 10.00 | 9.0 | 19.2 | 10.09 | 0.9 |
| 10.00 | 13.5 | 19.3 | 10.15 | 1.5 |
| 75.0 | | 86.9 | 75.0 | |
| 75.0 | 4.5 | 87.0 | 75.2 | 0.3 |
| 75.0 | 9.0 | 87.1 | 75.3 | 0.4 |
| 75.0 | 13.5 | 87.3 | 75.6 | 0.8 |
| 10.00 | | 18.0 | 10.00 | |
| 10.00 | Na 3.5 | 18.5 | 10.35 | 3.5 |
| 10.00 | 7.0 | 18.9 | 10.65 | 6.5 |
| 10.00 | 10.5 | 19.2 | 10.85 | 8.5 |
| 75.0 | | 89.0 | 75.0 | |
| 75.0 | 3.5 | 89.5 | 75.5 | 0.7 |
| 75.0 | 7.0 | 90.5 | 76.6 | 2.1 |
| 75.0 | 10.5 | 91.2 | 77.3 | 3.1 |

## TABLE III

THE INFLUENCE OF K ON THE RESULTS OF DETERMINATION OF Na

| *Analysis No.* | *Added 20 mg K to standard (% Na)* | *Added 0.08 mg K to standard (% Na)* | *Error calculated on the basis of the 20 mg K standard curve (rel. %)* |
|---|---|---|---|
| 1 | 0.0057 | 0.0073 | 28 |
| 2 | 0.0830 | 0.0918 | 11 |
| 3 | 0.0115 | 0.0141 | 23 |

amounts are added to every dilution in preparing the standard solutions, the matrix should correspond closely to that in which the element to be determined occurs. The only anion in the standard solution is chloride, which is also the most predominant anion in the sample solution. (For preparation see below).

If the standard curves are plotted as concentration to percentage transmission, the curve will bend towards the concentration axis; this is largely due to the self-absorption effect. If, however, the log concentration is plotted against the log percentage transmission, the curve will be an approximately straight line (Fig. 1). In order to test the reproducibility of the method, the same plant sample was analysed altogether 8 times, at intervals of several days, the results are shown in Table IV. All the replicates in Table IV are replicate weighings. The reproducibility of the readings on the same solution is of course better.

When the readings of a few standards were repeated over a longer period of time, it was found that they varied to a certain extent. As a consequence, standard curves must be drawn for every series of analyses and this is best accomplished by first reading half of the analysis series, then reading two or three standard solutions which cover the concentration range, and finally reading the rest of the series. It may be necessary as a last step to read an additional standard, if some of the values in the latter half of the series are not covered by the first reading of standards.

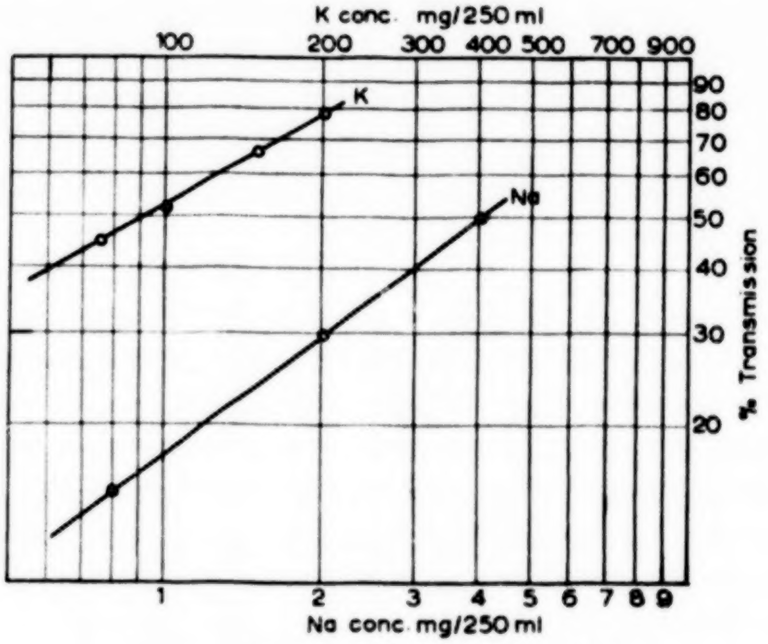

Fig. 1. Standard curve for K and Na.

TABLE IV

REPLICATED ANALYSES OF Na AND K DEVIATIONS

| *Element* | *Mean value* % | *Standard error of mean* % | *Variation* % | *Resulting analysis error rel.* % |
|---|---|---|---|---|
| Na | 0.126 | 0.0011 | 0.120–0.130 | ±1.8 |
| K | 1.61 | 0.0288 | 1.48–1.72 | ±3.6 |

It is also important that the process should be carried out without interruption, for instance between reading of samples and reading of standards. If the photometer is switched off during the process, one analysis must be repeated in order to check whether the reading has changed. If so, all preceding analyses must be repeated. Some analyses carried out with a voluntary stop between reading of the sample and reading of the standards revealed the possibility of a considerable error.

In order to discover whether interfering effects other than those compensated for were present, a series of recovery analyses was carried out. To six analysed samples, different amounts of potassium and sodium were added as chlorides, giving a recovery of about 100%, varying between 99–101% for potassium, and between 96–102% for sodium. The results show that probably no other essential enhancement effect is present, for this would also act upon the added amount of ions. It must be kept in mind, however, that a satisfactory recovery is not in itself a proof of reliability. A lowering effect caused by an ion which forms a difficulty dissociated compound with the element being analysed, will thus not always be revealed, if the amount of the interfering ion is small so that only a minor part of the element to be determined reacts. In that case, all the added amount will still be free and the recovery test may give a 100% result. This is, however, improbable for the sodium–potassium determination. (For calcium determination see below).

### DETERMINATION OF CALCIUM

Although many rapid and reliable chemical methods for determination of calcium are known, much work has been done to find a reliable method for flame photometric determination. The difficulties are far greater than in the determination of sodium and potassium. Calcium lines which are sensitive enough for the determination in plant material do exist, but cations as well as anions may interfere strongly. Many methods have been reported for the elimination of such interfering effects. The agreement between the different authors is not always good, probably owing to different experimental conditions. Baker[13] has examined the influence of different anions upon the calcium emission and concludes that phosphate, perchlorate and sulphate are the most important. Iron, aluminium and phosphate interfere[14–16] but can be precipitated with hexamethylenetetramine–ferric chloride[14], zirconium oxychloride[16] or ammonium acetate solution[15]. The last precipitant only removes the aluminium and iron, and the effect of phosphate is buffered by the addition of phosphate to sample and standard. Kick[17] also found interference from aluminium and phosphate and removed both by the addition of ammonia. Gjems[18] precipitated aluminium as benzoate, Schneider[19] precipitated phosphate with a solution of ammonium citrate and magnesia (4 : 1), and Adams[20] entirely eliminated the interfering anions with an ion exchange column.

Some authors describe methods which render possible a direct determination of calcium in plant ash extracts, without any preceding precipitation, *e.g.* Brown[5,21] and Pienaar[10], both of whom used a Beckman flame photometer of a direct reading type, with a photomultiplier. These authors used compensated standard solutions, and Brown completely eliminated the sodium interference by a didymium filter. Shoja[12] compensated for sodium, potassium, manganese and magnesium by standard solutions containing "exactly" the same amount of these elements as does the plant ash extract. Scharrer[22] eliminated the influence of phosphate, sulphate and nitrate by adding these ions to the plant ash solutions as well as to the standard solutions (radiation buffer technique).

A third method of avoiding interferences is to precipitate calcium, dissolve the precipitate and read the solution in the flame photometer. Amongst others, Puffeles[23] and Riehm[24] describe this method, precipitating calcium as oxalate.

In order to ascertain the magnitude of the interferences under our conditions, a direct determination of calcium in plant ash extracts was tried, using a standard containing only calcium chloride. The results were only half those obtained by different chemical methods. The proportion between the different values was in good agreement with the proportion between the chemically determined values, and an interesting fact was that the recovery was nearly 100%. This reveals the risk of uncritically using the recovery results as a measure of the reliability of a method.

Because of the high interference effects it would probably be difficult to compensate for these by using standard solutions containing added amounts of the interfering agents, and tentative experiments gave doubtful results. Removal of the interfering elements by precipitating procedure is unsatisfactory because of the risk of contamination, if the reagents are not quite free of calcium, and because it is impossible to remove all the interfering agents, except by very complicated procedures. If precipitation must be included it seems better to precipitate calcium for instance as oxalate, dissolve this, and then read the solution.

This procedure was submitted to a thorough examination, in order to ascertain whether it could compete with chemical methods in rapidity as well as accuracy. The gas mixture and pressures were as for the sodium–potassium determination, and the line 622 mμ was selected as the most suitable. From readings of calcium chloride solution in the photometer, the following parameters appeared to be the best:

| | |
|---|---|
| *Slit* | 0.3 mm |
| *Sensitivity* | midpoint |
| *Selector Switch* | 0.1 |
| *Phototube* | Red sensitive |
| *Load resistance* | 10,000 Me.ohm |

The solution obtained after dissolution of calcium oxalate in hydrochloric acid contains the ions of calcium, chloride and oxalate. The influence of the oxalate ion on the reading of calcium could enhance the latter by up to 12%. In this case, however, the interference causes no difficulties, as it is easy to prepare a standard solution with exactly the same composition as the analysis solution (see below).

TABLE V

DETERMINATION OF Ca BY DIFFERENT PROCEDURES, AND AFTER DIFFERENT METHODS OF WASHING OF PRECIPITATE

| *Washing procedure* | *Flame photometric method* (%) | *Permanganometric method* (%) | *Gravimetric method* (%) |
|---|---|---|---|
| Not washed | 0.478 | 0.514 | 0.499 |
| 3 times with $H_2O$ | 0.471 | 0.475 | 0.492 |
| 3 times with $NH_4Ox$ | 0.476 | — | 0.497 |
| 15 times with $H_2O$ | 0.466 | 0.475 | 0.481 |
| 15 times with $NH_4Ox$ | 0.468 | — | 0.491 |

No recovery tests were performed, but a comparison between the flame photometric, a titrimetric and a gravimetric (determination as CaO) method was made.

About 70 analyses were carried out, in which calcium was precipitated as oxalate. Out of these 70 precipitates, 1/5 were washed 3 times on the filter with distilled water, 1/5 were washed 3 times with a weak solution of ammonium oxalate, 1/5 were washed 15 times with distilled water, 1/5 were washed 15 times with the weak solution of ammonium oxalate, and the last 1/5 were submitted to no washing process. The different "types" of precipitates were analysed according to the three above methods (Table V). The deviations of replicates were not more than 0.5%. The flame photometric results were in good agreement with the results of titration with permanganate for the washed precipitates. The gravimetric results were about 4% higher. If the time-consuming washing process is omitted in the flame photometric procedure, this is considerably more rapid than either the titrimetric or the gravimetric procedure.

## RECOMMENDED PROCEDURE

The final, comprehensive procedure for the determinations of sodium, potassium and calcium in plant material is given below.

5 g of oven-dried material is weighed into a wide silica basin and ashed at 450° for 1½–2 h. The ash is taken up twice in 10 ml of 6 *N* hydrochloric acid and evaporated to dryness. To the residue is added 10 ml of 2 *N* hydrochloric acid, the basin is covered with a watch-glass and digested on the steam-bath for 30 min. After the watchglass has been rinsed the content of the basin is filtered through a Schleicher and Schüll filter paper No. 589² into a 250-ml volumetric flask and, after washing of the filter, made up to mark.

From this solution, 50 ml is taken for the direct determination of sodium and potassium and the rest is used for determination of calcium by the following procedure. The solution is heated to about 80° and a few drops of methyl red are added, followed by 15 ml of saturated ammonium oxalate solution. Ammonia (15%) is added until the colour changes, and the precipitate is set aside overnight or on the steam-bath for about 2 h. The solution is filtered through a Schleicher and Schüll filter paper No. 589³ without washing, the filter is perforated by a glass rod, and the precipitate is washed down into the precipitating beaker. The filter paper is rinsed off with 15 ml of 3 *N* hydrochloric acid and finally with water. After dissolution of the precipitate, the solution is transferred to a 250-ml volumetric flask, made up to mark, and is then ready for the flame photometric determination of calcium.

### *Preparations of the standard solutions*

#### *Stock solution for added elements*

*A*. 3125 mg $CaCO_3$ dissolved in 11.5 ml 6 *N* HCl and diluted to 500 ml, gives 25 mg Ca/10 ml; *B*. 3762.5 mg $MgCl_2 \cdot 6\ H_2O$ dissolved in 500 ml distilled water, gives 9 mg Mg/10 ml; *C*. 7635.0 mg KCl dissolved in 500 ml distilled water, gives 80 mg K/10 ml; *D*. 381.2 mg NaCl dissolved in 500 ml distilled water, gives 3 mg Na/10 ml.

#### *Sodium*

1016.59 mg NaCl dissolved in water and diluted to 1000 ml, gives 20 mg Na/50 ml. This solution is diluted to give separate 250-ml solutions containing respectively 10.0, 6.8, 4.0, 2.0 and 0.8 mg Na/250 ml. To every dilution is added 10 ml of each of the stock solutions A–C, before making up to mark.

*Potassium*

1.90692 g KCl dissolved in water and diluted to 1000 ml, gives 1 mg K/ml. This solution is diluted to give 250-ml solutions containing respectively 200, 150, 100, 75, 50, 25, 10 and 5 mg K/250 ml. To every dilution is added 10 ml of each of the stock solutions A, B and D, before making up to mark.

*Calcium*

3.64571 g $Ca(OOC)_2 \cdot H_2O$ dissolved in 75 ml 6 *N* HCl and diluted to 1000 ml, gives 1 mg Ca/ml. The solution is diluted to give 250-ml solutions containing 100, 75, 50, 25, 10, 5 and 2 mg Ca/250 ml, sufficient hydrochloric acid being added to give a concentration of 15 ml of 3 *N* HCl in each final solution.

8 samples could be analysed for sodium, potassium and calcium in about 8 h. This included 3.5 h for actual work in weighing, filtering, dilution and reading, the rest being required for ashing, evaporation, etc. The reading on the photometer takes only 15 min for all these three elements, provided that two series of analyses are prepared. The reading of the 16 analyses will then take 30 min, and time is saved in reading of the standards and setting of the instrument.

It is possible that a complexometric titration, for instance with EDTA, will be equally or more rapid for a simple calcium determination, but if determinations of sodium, potassium and calcium are required the flame photometric method is clearly preferable.

## ACKNOWLEDGEMENT

The author wishes to express his gratitude to The Agricultural Research Council of Norway for the financial support, to Prof. FREDR. ENDER for his permission to carry out the work and for his interest in it, and to Miss ANNA-ELISE HOLM for carrying out many of the analyses.

## SUMMARY

The flame photometric determination of sodium and potassium in plant ash extracts has been studied with particular reference to interferences; the instrument used was a Beckman spectrophotometer model DU, with a flame attachment of the total consumption burner type. The ions Na, K, Ca, Mg, $NO_3^-$, $PO_4^{-3}$ and $SO_4^{-2}$ were tested; sodium and potassium had a strong mutual enhancement effect which could cause errors up to 25%, but which could be compensated by adding the interfering elements to the standards. Interference effects prevented the direct determination of calcium in plant ash extracts, hence calcium oxalate was precipitated and dissolved and the solution was read in the flame photometer. This method was preferable to chemical methods particularly when sodium and potassium were to be determined in the same sample.

## RÉSUMÉ

Les auteurs ont examiné le dosage du sodium, du potassium et du calcium dans des extraits de plantes, par photométrie de flamme. Le calcium est séparé comme oxalate. Ce procédé est plus avantageux que les méthodes chimiques, en particulier lorsque le sodium et le potassium sont à doser dans le même échantillon.

## ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Bestimmung von Kalium, Natrium und Calcium in Pflanzenextrakten durch Flammenphotometrie. Da Kalium und Natrium die Bestimmung des Calciums stark stören, scheidet man dieses als Oxalat ab und bestimmt darin den Calciumgehalt. Im Filtrat werden dann Kalium und Natrium bestimmt.

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# A BASIS FOR THE DETERMINATION OF DISSOLVED OXYGEN BY ELECTRON SPIN RESONANCE SPECTROSCOPY*

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(Received April 6th, 1961)

## INTRODUCTION

A phenomenon has been observed which could provide the basis for a convenient method of quantitative analysis for dissolved oxygen in organic liquids. This method should be useful at dissolved oxygen concentrations as low as $10^{-5}$ *M*. A lower limit recently reported for gas chromatographic determination of dissolved oxygen in lubricating oil[1] is 20 times higher.

## EXPERIMENTAL

A system convenient for displaying the principle of the method is the following: A sample of irradiated coolant* was taken from an organic moderated and cooled reactor (the OMRE)[2]. This sample contained 31% of a residue which boiled significantly higher than the original commercial terphenyl with which the reactor was charged. The coolant sample was passed through a coarse sintered glass filter and the filtrate was used as a source of free radicals for the experiments to be described in this paper. One part by volume of the coolant filtrate was dissolved in two parts by volume of isopropyl biphenyl.

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* Work performed under AEC Contract AT-(11-1)-GEN-8.

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The peak height of the electron spin resonance (ESR) absorption spectrum of this solution was measured using a Varian Associates' ESR Spectrometer Model #4500 at different microwave power levels and at different partial pressures of oxygen gas in equilibrium** with the sample. (See Fig. 1. The height of the control peak of the ESR spectrum of an air-saturated benzene solution of 1,1-diphenyl-2-picrylhydrazyl (DPPH) of convenient concentration as a function of microwave attenuation is included in Fig. 1 for reference purposes). It was observed that the dependence of the peak height on the microwave power was dependent on the dissolved oxygen concentration. It is this change in the sensitivity of the peak height to microwave power with the concentration of dissolved oxygen that can be used to measure oxygen.

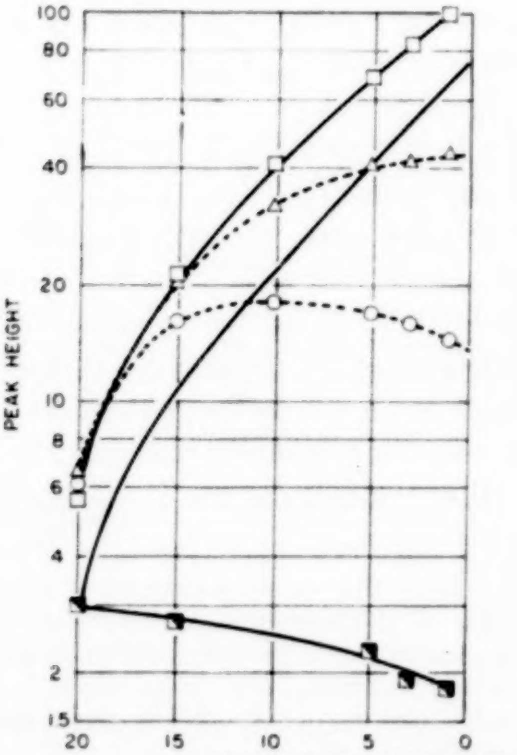

Fig. 1. Peak height of ESR absorption of OMRE coolant filtrate solution *vs.* microwave power at various $O_2$ partial pressures. □ # 4 (740 mm $O_2$), $4.8 \cdot 10^{-3}$ *N* in $O_2$. ——— DPPH solution. △ # 3 (105.4 mm $O_2$), $6.9 \cdot 10^{-4}$ *N* in $O_2$. ○ # 2 (18.3 mm $O_2$), $1.2 \cdot 10^{-4}$ *N* in $O_2$. ◥ specimen # 1 (0 mm $O_2$ partial pressure).

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* Although organic coolant was used as a sample in our laboratory, the method of analysis may be satisfactorily employed with other organic systems providing these systems meet the specifications discussed later in this paper.

** The sample was agitated and allowed to stand for 12 h with several $cm^2$ of surface of the ~1-ml sample in contact with the oxygen before the spectra were taken.

## RESULTS AND DISCUSSION

In Fig. 1 the log of the peak height* of the ESR absorption of the free radicals from the coolant is plotted *vs.* the log of the microwave power (in db) at various partial pressures of oxygen in the sample. It can be seen from this figure that small changes in the quantity of dissolved oxygen change the slope of the curve markedly in some specific range of power. For example, increasing the microwave power about 5 db (from 20 db attenuation to 15 db attenuation) reduces the peak height of a degassed sample by a factor of 0.9. However, increasing the microwave power over the same range increases the peak height of a sample equilibrated with 18.3 mm of oxygen by a factor of 2.7.

This effect of oxygen is completely reversible, *i.e.*, upon readmitting air to the sample which has been evacuated and shaking it to provide contact between the oxygen and the sample, the signal returns to the same level as was observed before evacuation.

The peak height is independent of oxygen pressure at sufficiently low power. In Fig. 1 at the lowest power easily available in our instrument (20 db attenuation) the peak height is independent of oxygen concentration within experimental error down to about $10^{-4}$ normal in oxygen. At lower concentrations still lower power would be required to make the peak height independent of oxygen concentrations.

The effect of oxygen concentration on the free radical signal is probably not due to chemical interaction of the oxygen with the free radicals as has been proposed for analogous systems. (For a discussion of the effect of oxygen on the ESR spectra of a number of free radicals in a variety of systems, see INGRAM[3]). The fact that at sufficiently low power the signal is independent of oxygen is sufficient proof that the oxygen has no effect on the free radicals in a chemical sense. Why does the oxygen affect the signal only at higher powers?

The explanation of this phenomenon almost certainly involves a deviation from equilibrium distribution of spin states which occurs at higher microwave powers[4]. This deviation from equilibrium is caused by the absorption of microwave power in the sample and is called saturation**. Saturation is less in the presence of oxygen because oxygen is paramagnetic and therefore catalyzes the interconversion of spin states[5]. That is, oxygen decreases the relaxation time and thereby reduces saturation***.

Some comments are in order concerning the requirements of a system to be used in analysis for oxygen based on the change in relaxation time of a free radical in the presence of dissolved oxygen. The first requirement is that the free radical chosen should saturate in the absence of oxygen at microwave powers easily available on the ESR spectrometer to be used (DPPH, for example, saturates in the absence of oxygen only enough to reduce the peak height to about 1/3 its unsaturated value at the highest microwave power available on our instrument).

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* Peak height has been calculated in this paper by dividing the difference between maximum and minimum chart paper values of the absorption derivative curve presented on the recorder by amplification settings of the output control unit, and multiplying this quotient by the line width (*i.e.*, the distance between maximum and minimum values on the derivative curve) measured in gauss and multiplying by $10^{-3}$. Assuming constant line shape, this value should be proportional to the actual absorption peak height.

** In electron spin resonance experiments the microwave radiation induces transitions between the two spin states of the free electron. At thermal equilibrium, the number of electrons in the upper energy (spin) state is smaller than the number in the lower state. Since the transition probabilities are identical, the number of upward transitions is greater than the number of downward transitions, resulting in a net absorption of energy from the microwave field. If the surroundings can not take away energy from the excited spin states fast enough to maintain an equilibrium (Boltzman) distribution between the two spin states, the signal observed will be reduced. For a more detailed discussion of electron spin resonance and saturation effects, see INGRAM[3].

*** The DPPH solution which was open to the air does not saturate in the range of microwave power levels that were used in these experiments. The data for this solution falls on a line parallel to line #4 (within experimental error) indicating no saturation of the coolant in equilibrium with 740 mm of oxygen.

A second requirement for a convenient system is that the free radical used be stable in solution in the sample even in the presence of oxygen.

The actual analytical method would involve some technique for adding degassed free radical* to the organic sample without exposing it to conditions that would change the oxygen content. For some applications, an evacuated tube containing the free radical might be immersed into a liquid sample and the sample admitted through a valve. The solution could be stirred from the outside to insure homogeneity.

Less than 1/4 ml of sample would be required and after calibration the analysis would require less than one man hour unless greater accuracy or sensitivity is desired than we are claiming for the method.

## SUMMARY

The ESR spectrum of certain free radicals in solutions is strongly affected by dissolved oxygen. This phenomena can be used as a basis of a simple method for the determination of molecular oxygen in organic solutions. It should be of particular value in the quantitative determination of low concentrations of oxygen, *i.e.*, in the region of $10^{-5}$ to $10^{-3}$ normal.

## RÉSUMÉ

Le spectre de résonance du spin de l'électron de certains radicaux libres en solution est fortement modifié par l'oxygène dissous. Ce phénomène a permis d'établir une méthode simple pour le dosage de l'oxygène moléculaire dans des solutions organiques.

## ZUSAMMENFASSUNG

Das Elektronen-Spin-Resonnanz Spektrum gewisser freier Radikale in Lösung wird durch gelösten Sauerstoff stark beeinflusst. Dieses Phänomen kann als Grundlage einer Methode zur Bestimmung von molekularem Sauerstoff in organischen Lösungen verwendet werden.

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* The quantity of free radicals is not important since the change of signal with microwave power is the significant quantity.

# RADIOMETRIC TRACE ANALYSIS*

## QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH PHOSPHATE-$^{32}$P

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(Received March 30th, 1961)

### GENERAL INTRODUCTION

The name "radiometric analysis" is often used for the measurement of the amount of a nucleide by means of its radio-activity, but in the opinion of the present author, this term should be reserved for analytical methods in which induced or added radio-activity is applied. Of these methods isotope dilution and activation-analysis are specially important, the latter requiring a strong source of nuclear particles, the former being in fact merely a make-shift, the sensitivity of the analysis depending on an *addition* technique.

The term radiometric analysis is often reserved for three other types of analysis. The first (*1*) and most widely applied, uses the radio-active tool merely as a ***tracer*** to denote the end-point or the starting point of a reaction; as with isotope dilution the sensitivity is in principle restricted**. Both other techniques, (*2*) analysis with radio-active reagents and (*3*) analysis by exchange-reactions involving radio-active isotopes, do not suffer from this disadvantage. A survey of the literature[1] revealed that, notwithstanding this, both methods (*2*) and (*3*), but especially method (*3*), are less popular than method (*1*).

Preliminary experiments[1] led to the choice of (*a*) phosphate-$^{32}$P for the quantitative paper chromatography of traces of metals — the application to lead is described below — and (*b*) the exchange reactions of the system: metal ion in water–metal–diethyldithiocarbamate complex in chloroform for the determination of traces of metals in solution. Applications of the latter system to lead and cobalt will be described in later papers.

### QUANTITATIVE PAPER CHROMATOGRAPHY OF LEAD WITH PHOSPHATE-$^{32}$P

#### *Introduction*

Phosphate-$^{32}$P has been used in the analysis of metals by SUE[2], LANGER[3], MOELLER AND SCHWEITZER[4], BARCIA GOYANES[5], TANANAEV[6] and MEVEL[7]. Filter paper was not used by these authors. It was chosen as a medium for our experiments because a

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* Publication 124a of the Research Institute for Animal Husbandry "Schoonoord".

** Method (*1*) is mostly carried out as a titration with a radio-active indicator and a non-radio-active reagent. It can be made more sensitive by using a radio-active reagent, but this converts method (*1*) to a special form of method (*2*).

*Anal. Chim. Acta*, 25 (1961) 570–578

higher sensitivity could be expected. Interferences from other metals could have been diminished by a proper choice of pH and masking agents, but a much better selectivity was obtained by the development of a paper chromatogram to yield a separation of the relevant elements.

Phosphate-$^{32}$P is a rather general reagent for metals. Thus procedures are indicated here for two cases: (*1*) in which only lead is of interest, and (*2*) in which other ions are also of interest. Only case (*1*) is worked out in detail.

## *Experimental*

### *Materials*

*Phosphate-$^{32}$P solutions*: (*a*) 1% $Na_2H^{32}PO_4$ in water; 10 $\mu$C/ml; (*b*) Solution (*a*) 4 times diluted.

*$^{210}$Pb solution*: 400 $\mu$g of $^{210}$Pb (Ra-D in equilibrium with its decay products) and 4 $\mu$C per ml of 1 *N* nitric acid.

*Other solutions of radio-active metals* were prepared in a similar way. All were kept in polyethylene vessels. The radio-activity was measured periodically, to control losses by adsorption to the wall.

*Ion exchange water* was used which had a resistivity of more than 3 to 4 Megohms.

Hydrochloric acid ($d = 1.18$), nitric acid ($d = 1.42$), ammonia ($d = 0.88$) and methanol were "AnalaR"; ethanol, *n*-propanol and hydrogen peroxide (30%) were "Merck p.a.".

*Borax–oxalate buffer*: Mix 60 ml of ethanol, 60 ml of *n*-propanol, 20 ml of water, 40 ml of 0.05 *M* borax and 20 ml of 0.05 *M* oxalic acid and adjust to pH 8.0 with the borax solution.

As the isotope $^{32}$P emits hard $\beta$-rays, measurement in filter paper does not involve any difficulty. *The counting equipment* consisted of an end-window GM-tube (Philips 18506), a scanner-sample changer (Phys. Lab. Univ. of Utrecht) and a scaler-ratemeter (Philips). The usual precautions for radioactive tracer work *and* for trace analysis were taken. Lead-210 was measured by the $\beta$-radiation of its daughter $^{210}$Bi. A check was made after 5 days ($= \tau\frac{1}{2}$ of $^{210}$Bi).

*pH-values* were measured with a Beckman model-G instrument, calibrated on aqueous standards. Ordinary chromatographic sprayers and dry boxes were used for spraying the phosphate-$^{32}$P solution. The papers were either Whatman no. 1 or Schleicher and Schüll 2043 b.

### *Pretreatment of the sample*

The sample — or its ash — is dissolved in a minimum volume of nitric or hydrochloric acid. The amounts of these acids must be kept small, as even the AnalaR reagents contain some lead. Complexing agents should be absent; they can be destroyed for instance by ashing with 1 : 1 nitric acid–hydrogen peroxide.

The sample should contain at least 1 $\mu$g of lead. Foreign cations and anions are allowed in amounts up to a few hundred micrograms. Larger amounts tend to overload the paper.

### *Application to the paper*

The application of milliliter amounts of aqueous solutions to the paper is not practicable. Some methods have been devised, for instance by PHILLIPS[8] and by

FRENCH AND GIBSON[9], but for a routine method they are too cumbersome. Thus the solution usually has to be concentrated by evaporation.

The method of THIERS *et al.*[10] proved to be preferable. The final volume should be about 0.05 to 0.1 ml, the estimation of which is a matter of practise. If a dish becomes dry or precipitation occurs, dilute hydrochloric acid should be added; organic residues are ashed with 1 : 1 nitric acid–hydrogen peroxide. It is not absolutely necessary to produce a small spot on the paper although a somewhat better chromatogram would result. A larger spot was accepted and the paper was dipped into the solution, this being the most convenient method. The efficiency of the method was tested with $^{210}$Pb: 97 to 99% of the lead was found on the paper (as compared with direct administration).

From the literature, and from our preliminary experiments with other radio-active reagents, it was clear that appreciable amounts of several metals are contained in chromatographic paper. Although the greater part of these metals consists of Fe, Ca, Al, Mg and Cu, the use of a purified paper proved to be of advantage in our experiments with amounts of lead smaller than 3 $\mu$g. Investigations on the method of purification are described elsewhere[1]. The method of choice is given below.

Cut strips of paper (2.5 or 3.0 × 30 cm) and hang them in a chromatographic jar; rinse for 24 h with 9 : 1 methanol–concentrated hydrochloric acid in the descending way; remove the eluate and ventilate the jar for a few hours. Then run for 24 h with 9 : 1 methanol–ammonia, ventilate and run for 24 h with 95 : 5 methanol–water. Allow to dry in the atmosphere of the last solvent.

The second solvent re-establishes the pH and the third one the water content of the paper. Several paper chromatographic separations with these papers proved to give essentially the same results as with untreated paper.

(*1*) When only lead is to be determined, the sample is placed on a strip of paper as indicated above and the ions are separated as described in the next paragraph.

(*2*) When other cations are to be determined as well and the corresponding spots are separated by less than 4 cm, a sheet of paper — 20 × 20 cm — is used instead of the paper strip. The dipping technique is somewhat more difficult here; satisfactory results are obtained however, when the paper is folded twice (Fig. 1) and the tip is immersed in the evaporation dish. A more or less irregular spot forms around the intersection of the two folds. When the solution is placed on the paper with a pipet, a more rectangular spot can be formed (Fig. 2), which has some advantage in connection with the subsequent chromatographic separation.

(*3*) When other cations are to be determined as well, but the corresponding spots are separated by 4 cm or more, a paper strip is used.

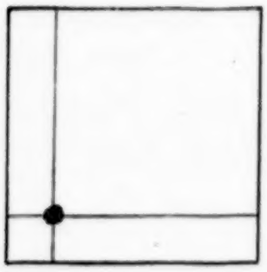

Fig. 1. Application of the sample by dipping.

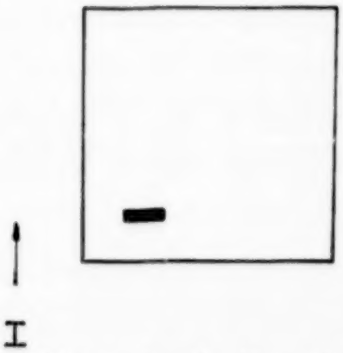

Fig. 2. Application of the sample with a pipet.

### *Paper chromatographic separation of lead*

*(1) When lead is the only element to be determined*, the only requirement for the solvent used for the development of the chromatogram is that it should separate lead from interfering cations and anions. The choice of this solvent depends on the composition of the sample. Directions are given here for the ash of 50 mg of dry cow liver, which contains at least 1 µg of lead.

For this sample the alcoholic solvents used by LEDERER[11], WALKER AND LEDERER[12], BURSTALL *et al.*[13] and HUNT[14], were found to be the most convenient. These authors were able to separate $Pb^{+2}$ from $Fe^{+3}$, $Zn^{+2}$, $Cu^{+2}$, $Mn^{+2}$, $Co^{+2}$, $Tl^{+3}$, $Tl^{+}$, $Hg^{+2}$, $Zr^{+4}$, $Ag^{+}$, $Al^{+3}$, $Mg^{+2}$, $Ni^{+2}$, $Sn^{+2}$, $Bi^{+3}$, $Cd^{+2}$ and $MoO_4^{-2}$, but not from $Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$, $Ce^{+3}$, $Th^{+4}$, the rare earths and $Hg^{+}$.

In our own experiments the cations $Fe^{+3}$, $Cu^{+2}$, $Zn^{+2}$, $Mn^{+2}$, $Co^{+2}$, $Tl^{+3}$, $Tl^{+}$, $Hg^{+}$, $Hg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$, $Al^{+3}$ and $Mg^{+2}$ were tested, as well as the anions $PO_4^{-3}$, $MoO_4^{-2}$ and $SO_4^{-2}$. Paper strips with these ions, in amounts ranging from 1 to 200 µg, were chromatographed in the ascending way with the solvent 9:1 ethanol–5 *N* hydrochloric acid.

The radioisotopes $^{59}Fe$, $^{65}Zn$, $^{54}Mn$, $^{60}Co$, $^{204}Tl$, $^{203}Hg$, $^{45}Ca$, $^{89}Sr$, $^{99}Mo$, $^{32}P$, $^{35}S$ and $^{210}Pb$ were used to detect the respective ions. The ions $Cu^{+2}$, $Ba^{+2}$, $Mg^{+2}$ and $Al^{+3}$ were detected by the tests described by POLLARD AND MCOMIE[15].

The main part of the lead was found at $R_F$ 0.15 (with 1 to 3 µg of lead the size of the spot was about 1 cm²) but 0.09 ± 0.03 µg of lead were eluted and found at higher $R_F$ values.

$Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$, $Hg^{+}$ and $Tl^{+}$ could not be separated from lead. The last two ions can easily be oxidized before the chromatographic separation and then do not interfere; thus only the ions $Ca^{+2}$, $Sr^{+2}$ and $Ba^{+2}$ interfere seriously. For biological material only calcium is of much importance.

*(2) If the determination of other cations* is also required, the separation should be carried out (on the paper sheet) with another solvent, as the alcoholic solvent used above will in general not produce mutual separations of these other cations. The choice of the solvent depends on the ions of interest.

With most solvents, the alkaline earth ions are separated from lead and need not be considered further. On the other hand, with no other solvent tested was the separation of lead from large amounts of other heavy metals as good as with the alcoholic hydrochloric acid used in case (*1*).

### *Reaction with phosphate-$^{32}P$*

(*1*) After the paper chromatographic separation of $Pb^{+2}$, the paper was dried and neutralized in ammonia vapor. By this treatment the pH was increased to about 4.5. The paper was then sprayed (on both sides) with one of the phosphate-$^{32}P$ solutions, the choice depending on the amount of lead expected.

Spraying was carried out in a dry box or in an efficient hood; it did not involve any danger to the operator when the walls were covered with absorbing paper. The paper must not be sprayed too heavily, otherwise the solvent drips off and the spots spread. It is also possible to apply the reagent with a pipet or a small paint brush, but these methods give somewhat less satisfactory results.

(*2*) When other metals were to be determined (and the successive spots were separated by less than 4 cm), after drying and neutralization, the developed part only (Fig. 3) was sprayed with the phosphate-$^{32}$P, the rest being masked with a screen.

(3) When the spots were separated by more than 4 cm, the paper was cut into pieces containing the different spots .To these pieces technique (*1*) was applied.

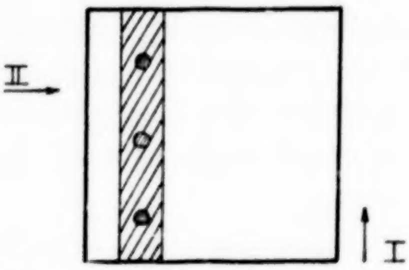

Fig. 3. Spraying of a paper sheet with phosphate-$^{32}$P.

*Separation from excess $^{32}PO_4^{-3}$ and alkaline earth metals*

(*1*) After the strip had been dried from the spraying, the separating solvent (see below) was allowed to ascend in the same direction in which the chromatogram was developed. If some of the cations lying between $R_F$ 0.3 and $R_F$ 1.0 had to be detected, the strip was cut off at $R_F$ 0.3; the separating solvent was then applied in the descending way and allowed to drip off at the point $R_F$ 0.3.

The solvent for the elution of excess phosphate-$^{32}$P was chosen so as to elute the alkaline earth metals (not separated from lead above) as well. A borax – oxalate buffer was found to be suitable*; alcohol was added to diminish the solubility of the lead phosphate (see EBEL AND VOLMAR[16]). With this solvent only 0.04, 0.13 and 0.44% of the original calcium, strontium and barium respectively remained in the spot as the phosphate; only small amounts of lead (10%, St. dev. 1.5) were eluted, probably as the oxalate.

Another suitable solvent was found to be an alcoholic acetate buffer of pH 4.5: 0.7% of the calcium, strontium or barium were retained and only 6% of the smaller amounts of lead was eluted.

(*2*) In this case the elution is carried out perpendicularly to the chromatographic development (directions II and I in Fig. 3).

The composition of the eluting solvent depends on the chromatogram and the ions of interest. For example, borax – oxalate can be used for magnesium, zinc and manganese; borax alone is suitable for calcium, magnesium and many other metals (for calcium and magnesium alone a spray with 8-hydroxyquinoline is inserted).

(*3*) Here, different solvents can be used for the successive pieces of the chromatogram. The descending technique is used and the solvent is allowed to drip off.

*Measurement of the radioactivity of the lead phosphate-$^{32}$P*

After the separation of lead phosphate from excess of reagent and interfering metals, the paper is dried and cut off at $R_F$ 0.30. The part which contains the lead phosphate is folded lengthwise and fixed to a thick aluminium strip which is passed through the scanner.

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* Citrate and tartrate are not effective. Probably insoluble oxalates are formed.

Thus folded the paper is narrower than the window by a factor of 2 and the geometrical error caused by differences in the distribution of the activity is minimized. Less than 1% of the radiation from the lower half of the paper is absorbed. The total error caused by both effects is smaller than 3%.

The slit width and the scanning speed are regulated in accordance with the activity on the paper; usually a slit of 5 mm and a speed of 2 to 32 cm/h are sufficient to obtain a statistical error which is smaller than 3%. The total of all errors is about 3 to 4%.

The resulting curve is planimetered. After evaluation of the half-life correction, the amount of lead is found by comparison with standards.

## PROCEDURE

### (for case 1)

The procedure is given for a sample containing from 1 to 4 μg of lead and (per μequiv. of lead) not more than the following amounts of foreign metals (in μequiv.): 250 Ca, 70 Sr, 20 Ba*, 0.1 $Hg^+$, 0.1 $Tl^+$**, 0.1 $Ce^{+3}$ and 0.1 $Th^{+4}$***. Less than 1 mg of inorganic material should be present altogether†.

Dissolve in hydrochloric and/or nitric acid and evaporate to 0.05–0.1 ml. Prepare strips of acid-washed Whatman No. 1 paper, fold them at 6 cm from one end and dip the fold in the solution until the spot is about 5 cm²††. Dry while hanging on a glass frame in a clean atmosphere and dip again until all the solution is taken up (twice is mostly sufficient).

Dry for 60 min, condition in the vapor of 9:1 ethanol–5 *N* hydrochloric acid for 16 h and chromatograph with this solvent in the ascending way for 4 h (about 20 cm).

Dry for 60 min, neutralize in the vapor of concentrated ammonia for 30 min and ventilate for 15 min.

Spray the region of $R_F$ 0.1 to 0.2 with the $Na_2H^{32}PO_4$-solution (*b*) in a dry box the inside of which is covered with absorbing paper. Spray on both sides and to thorough dampness; about 1 ml is required per 80 cm²†††.

Dry again and allow the borax–oxalate buffer to ascend in the direction of the chromatogram. Dry, and determine the radioactivity in the region of $R_F$ 0.1 to 0.2.

## RESULTS

The blank amounted to 0.51 μg of lead (St. dev. 0.06) per cm² of acid-washed paper. This blank went up with (*1*) the surface area of the spot, (*2*) the amount of phosphate-$^{32}P$, (*3*) the amount of nitric acid–hydrogen peroxide applied. For factors (*1*) and (*2*) it did not go up in equal ratio to their increase. The blank for unwashed paper was 1 μg of lead (St. dev. 0.7) per cm².

The ions $Fe^{+3}$, $Cu^{+2}$, $Zn^{+2}$, $Mn^{+2}$, $MoO_4^{-2}$, $Co^{+2}$, $Al^{+3}$, $Hg^{+2}$, $Tl^{+3}$ and $Mg^{+2}$ in 100-μg amounts had no influence on the blank. The same amounts of $Ca^{+2}$, $Sr^{+2}$ and

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* With up to 4 times larger — but approximately known — amounts of Ca, Sr and Ba a "blank", determined with a simulated sample containing no lead, can be subtracted. Alternatively another solvent should be sought for chromatography.

** The interference of $Hg^+$ and $Tl^+$ is easily prevented by oxidation to $Hg^{+2}$ and $Tl^{+3}$ respectively.

*** With larger amounts of $Ce^{+3}$ and $Th^{+4}$ another solvent should be sought for chromatography.

† With thicker papers (*e.g.* Whatman No. 3 mm) larger samples can be handled.

†† With amounts of lead larger than 3 μg unwashed papers can be used.

††† Solution (*a*) is used for 4 to 16 μg of lead.

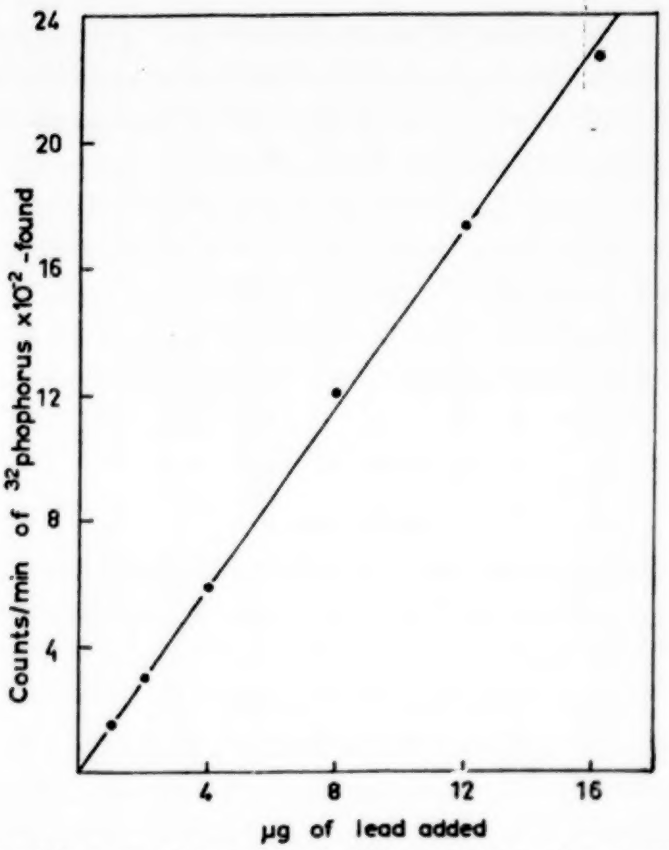

Fig. 4. Results with 1 to 16 µg of lead. (Mean values of 4 experiments each).

## TABLE I

### DETERMINATION OF 1 µg OF LEAD IN A CHROMATOGRAM

(Mean values and standard deviations of 3 experiments each)

| *Exp. No.* | *Foreign ions (µg)* | *Subtracted blank (µg of Pb)*[a] | *Lead found (µg)* | *Standard deviation (%)* | *Lead found, corrected value*[b] *(µg)* |
|---|---|---|---|---|---|
| 1 | Ca 100<br>Sr 20<br>Ba 20 | 0.91 | 1.03 | 11.5 | 1.12 |
| 2 | Fe 300<br>Cu 100<br>Zn 200 | 0.51 | 0.89 | 9.5 | 0.98 |
| 3[c] | Na 150 Mn 1<br>K 400 Fe 15<br>Ca 15 Cu 5<br>Mg 10 Zn 10<br>Mo 1 Co 0.1 | 0.54 | 0.95 | 11.0 | 1.04 |
| 4[c] | As in the preceding experiment<br>above: $PO_4^{-3}$ 30<br>$SO_4^{-2}$ 20 | 0.54 | 0.91 | 9.5 | 1.00 |
| 5 | $PO_4^{-3}$ 100<br>$SO_4^{-2}$ 100 | 0.51 | 0.92 | 8.5 | 1.01 |

[a] An extra blank, equivalent to 0.40 (St. dev. 0.06) µg of lead, can be calculated for experiment 1, and an extra of 0.03 µg of lead for experiments 3 and 4.

[b] For the loss of 0.09 µg of lead in the paper chromatographic separation.

[c] Cations (and in experiment 4: 2% of the anions) in the ash of 50 mg of dry cow liver, which generally contains more than 2 µg of lead.

$Ba^{+2}$ produced a blank corresponding to 0.2, 0.3 and 0.7 µg of lead respectively (St. devs. 0.05, 0.08 and 0.17).

Results with 1 to 16 µg of lead are shown in Fig. 4. Mean values of 4 experiments are given. Acid-washed papers were used throughout; the results for 8, 12 and 16 µg of lead obtained with unwashed paper were similar but the standard deviations were higher.

In Table I some examples are given of the determination of 1 µg of lead in a simulated biological ash.

The amount of lead is calculated from the $^{32}P$-value found (in a spot of 1 $cm^2$) in the absence of foreign ions and hence by omission of the paper chromatographic separation. Thus a correction for the loss of 0.09 µg of lead in this separation had to be made. On the other hand only the variations found in the loss of lead phosphate had an influence, while a correction for the 10% loss itself was not required.

Results with larger amounts of lead show smaller standard deviations, while a larger excess of foreign ions is allowed. As the latter tend to disturb the chromatogram by overloading*, these results are not very interesting: an aliquot of the sample containing at least 1 µg of lead should be taken.

## DISCUSSION

Combination with paper chromatography makes the radioactive reagent more selective and more sensitive. It now becomes applicable to several cations simultaneously.

Phosphate-$^{32}P$ is a very useful reagent in the quantitative paper chromatography of trace elements. The sensitivity is comparable with the polarographic and spectrophotometric (dithizone) techniques but the method is 5 times less sensitive than the spectrographic method. Our technique has the distinct advantage, however, that it is directly applicable to the paper. For metals like Fe, Mn, Zn, Ca, Mg etc. the sensitivity in µg will probably compare favourable with densitometric practise.

The ratio P/Pb can be calculated from the specific activity of the phosphate-$^{32}P$. As a mean of 10 experiments with 16 µg of lead, the value 1.10 (St. dev. 0.06) was found. Probably $PbHPO_4$ is precipitated at pH 4.5 (see above**) and excess $^{32}PO_4^{-3}$ is adsorbed or occluded. Repetition of the separation of phosphate-$^{32}P$ was found to decrease the P/Pb-ratio to 1.06 (St. dev. 0.035). The blank and its standard deviation were also lowered but 0.05 to 0.12 µg of lead was lost. Thus repetition of the separation did not increase the overall accuracy.

The effect of the borax–oxalate buffer is obviously due to the precipitation of alkaline earth oxalates.

When the phosphate-$^{32}P$ is sprayed on the "neutralized" chromatogram, lead phosphate precipitates but the pH of 4 to 5 will largely prevent the precipitation of the alkaline earth-phosphates. Separation of excess reagent with the borax–oxalate buffer of pH 8.0 causes precipitation of calcium, strontium and barium, partly as the phosphates but mostly as the oxalates. As the solubility products of the latter are smaller (for calcium by a factor of 2500) and as the concentration of the oxalate ion increases rapidly whereas the concentration of the phosphate ion decreases during the separation process, the greater part of the alkaline earth phosphates is finally transformed to the oxalates.

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* Larger amounts are permitted with Whatman No. 3 mm paper.

** HUBICKI *et al.*[17] found the solubility product of $PbHPO_4$ to be minimal at pH 4.5. The addition of alcohol decreased the solubility. $Pb_3(PO_4)_2$ was precipitated only above pH 6.

Owing to the change in the concentrations of the two anions, part of the lead phosphate is also transformed to the oxalate. The solubility products of both lead salts are comparable however; above, the process (which will undoubtedly be further modified by the paper and by the partly alcoholic medium) starts with a precipitate of the lead.

The experimental standard deviations can be totally accounted for by the factors known to contribute to them: (*1*) 0.015 $\mu g$ is due to variations in the transformation of lead phosphate described above, (*2*) 0.03 $\mu g$ is due to variations in the amount of lead lost in the paper chromatographic separation, (*3*) 0.06 $\mu g$ is due to the variable paper blank*, (*4*) 0.04 $\mu g$ is due to the error made in the measurement of $^{32}P$ and (*5*) 0.06 $\mu g$ is caused by the adsorption of the reagent on (or occlusion in) the precipitate. In experiment 1 (Table I) a factor (*6*) of 0.06 $\mu g$ due to variations in the alkaline earth blanks has to be added to this list.

ACKNOWLEDGEMENT

The author is indebted to Mrs. W. Cliné-Theil for valuable technical assistance.

## SUMMARY

A method is described for the selective determination of lead in paper chromatograms, down to 1 $\mu g$ (standard deviation 11%). After development and drying, the lead spot is sprayed with a $Na_2H^{32}PO_4$ solution and dried. Excess reagent and alkaline earth phosphates are eluted with a borax–oxalate buffer of pH 8.0. Eventually, the radio-activity of the lead spot is measured. The filter paper renders the method about 40 times more sensitive than existing radiometric techniques with phosphate-$^{32}P$. The method can be modified for the simultaneous determination of many cations.

## RÉSUMÉ

Une méthode radiométrique est proposée pour le dosage du plomb par chromatographie sur papier, au moyen de phosphate disodique, marqué au phosphore-32. La sensibilité est meilleure que celle obtenue avec les autres techniques radiométriques, à l'aide de $Na_2H^{32}PO_4$

## ZUSAMMENFASSUNG

Beschreibung einer radiometrischen Methode zur Bestimmung von Spuren von Blei durch Papierchromatographie unter Verwendung von Dinatriumphosphat-$^{32}P$. Auf mögliche Modifikationen zur gleichzeitigen Bestimmung mehrerer Kationen wird hingewiesen.

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* It can be shown[1], that the greater part of this blank is due to the adsorption of phosphate-$^{32}P$ to the paper.

# PREPARATION OF STOICHIOMETRIC $U_3O_8$*

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(Received April 12th, 1961)

A method was needed for preparing stoichiometric $U_3O_8$ for precise determination of uranium by gravimetric methods and for the preparation of uranium isotopic standards by the isotopic dilution method. VOSS AND GREENE[1] have determined the uranium in $U_3O_8$ prepared from uranyl nitrate, uranyl fluoride, and uranium trioxide and found that some of these compounds do not ignite to a stoichiometric $U_3O_8$ under the usual ignition conditions (800–850° for 1–3 h). BROUNS AND MILLS[2] have reported that uranium trioxide was not completely converted to $U_3O_8$ at 800°, "even after prolonged heating."

Non-stoichiometry is common with the uranium–oxygen compounds[3]; however, under properly controlled conditions, stoichiometric $U_3O_8$, which can be used as such in precise laboratory work, is produced. The ignition time and temperature necessary for the preparation of stoichiometric $U_3O_8$ are dependent upon the starting chemical compound (parent material) and the sample size (bed depth). Chemical alteration of the parent material, such as treatment with hydrofluoric acid, can change the required ignition conditions. Parent materials studied were uranium metal, uranyl fluoride, uranium peroxide, uranium trioxide, and uranyl nitrate. The ignition conditions for each will be discussed separately.

## EXPERIMENTAL

### *Apparatus*

The electric furnace had a safe operating temperature of 1360° and the muffle was heated uniformly by radiant heat from four bar-type resistance elements. The temperature was controlled to ±10° by a potentiometer and superheated steam was introduced in the rear of the furnace when needed. The top and sides of the muffle were lined with platinum. A calibrated potentiometer was used in checking the furnace temperature to assure accurate temperature control.

20-ml platinum dishes were used for all 10-g samples to standardize the bed depth.

A digital voltmeter with platinum–tungsten and platinum-saturated calomel electrode systems was used to determine the $U^{+3}/U^{+4}$ and $U^{+4}/U^{+6}$ end-points, respectively.

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

### *Procedure*

Three or four 10-g samples of the parent material as a group were ignited in platinum dishes in a furnace (without steam unless specified) for a period of time at a controlled temperature, removed from the furnace, cooled in a desiccator, and weighed. An empty platinum dish was processed as a blank with each group of samples. The oxides were ignited for specified times and temperatures and weighed after each ignition. The amount of uranium in each dish was determined by the precise potentiometric titration method after the last ignition. The uranium content of the oxide at each ignition step was then calculated from the known amount of uranium in each dish and the observed weight of oxide at each weighing to determine the variation of the uranium content as a function of ignition conditions. The results within a group were averaged to obtain a mean.

## RESULTS

### *Calculations*

All calculations were made using 238.038 as the chemical atomic weight of natural uranium, the material used in this study. This value is based on chemical atomic weights obtained by dividing the nuclidic mass of each isotope[4,5] by Nier's constant[6] and using 0.7115, 0.0055, and 99.283 for the weight percent of $^{235}U$, $^{234}U$, and $^{238}U$, respectively, in natural uranium.

In this paper "constant weight" is defined as a change no greater than 0.0001 g/10 g of sample after an ignition of not less than 2 h, and "theoretical value" refers to the uranium content of stoichiometric $U_3O_8$ which is 84.800 wt.% for natural uranium. The uranium values determined by the precise potentiometric titration method have precision limits for a single analysis of $\pm 0.015$ absolute at the 95% confidence level and are relative to the oxidizing power of the National Bureau of Standards Lot 136A potassium dichromate being 99.99% with a bias of $0.00 \pm 0.01\%$. Corrections have been made for the metallic impurities in the oxide.

### *Uranium metal*

Since some investigators have used uranium metal as the standard in the titration method, it was decided to compare the uranium content determined by titration with potassium dichromate to that of the weight of metal after correcting for metallic impurities. 8-g samples of metallic uranium were pickled in nitric acid to dissolve any oxide coating on the surface, dried with acetone, weighed, and converted to the oxide by ignition at 850° for 2 h. The concentration of uranium in the metal determined by titration using potassium dichromate as the standard was $99.976 \pm 0.017\%$. The

TABLE I

URANIUM IN $U_3O_8$ PREPARED FROM METALLIC URANIUM IGNITED FOR 2 h AT 850°

| *Sample No.* | *Uranium (wt.%)* |
|---|---|
| 1 | 84.794 |
| 2 | 84.792 |
| 3 | 84.790 |
| Mean | 84.792 |
| Percent of theoretical value | 99.991 |

concentration of metallic impurities in the metal obtained by a spectrographic analysis was 130 (+100%, −50%) p.p.m.; hence, by difference, the uranium content of the metal is between 99.974 and 99.994%. Since these values encompass the titration values, there appears to be no significant bias in the titration value based on dichromate. The amounts of sulfur and carbon in the metal were determined to be less than 10 and 50 p.p.m., respectively, and no correction was made for these impurities.

The uranium concentration of the oxide prepared from the metal was 99.991% (corrected for metallic impurities) of the theoretical value as shown in Table I.

### *Uranyl fluoride*

Samples of uranyl fluoride were ignited at 850° ± 10° for 16 h (the first hour in a steam atmosphere to prevent any loss of uranium from sublimation) and the average uranium content of the oxide by titration, shown in Table II, was the theoretical value. Ignition at 900° for 4 h converted samples of uranyl fluoride to stoichiometric $U_3O_8$.

TABLE II

URANIUM IN $U_3O_8$ PREPARED FROM URANYL FLUORIDE

| *Sample No.* | *Uranium (wt.%)* |
|---|---|
| *Ignited for 16 h at 850°* | |
| 1 | 84.798 |
| 2 | 84.793 |
| 3 | 84.793 |
| 4 | 84.815 |
| Mean | 84.800 |
| Percent of theoretical value | 100.00 |
| *Ignited for 4 h at 900°* | |
| 5 | 84.795 |
| 6 | 84.798 |
| 7 | 84.802 |
| 8 | 84.805 |
| Mean | 84.800 |
| Percent of theoretical value | 100.00 |

Small samples of uranyl fluoride, 300–400 mg, when ignited at 850° for only 30 min in a steam atmosphere produced an oxide that was stoichiometric. The formation of stoichiometric $U_3O_8$ with such a short ignition was probably due to the small sample size and the effect of the steam, since $U_3O_8$ samples which were ignited in a steam atmosphere gained weight (0.01 to 0.02%) when heated under identical conditions without steam. There was also a loss in the weight of $U_3O_8$ when changed from a dry to a steam atmosphere at 850°. Several of these small samples were combined for each titration.

### *Uranium peroxide*

Samples of uranium peroxide were converted to stoichiometric $U_3O_8$ by ignition at 850° ± 10° for 16 h and the results are shown in Table III.

A second technique used to convert uranium peroxide to stoichiometric $U_3O_8$ was ignition for 4 h at 1000°, followed by 2-h ignition periods (usually two) at 850° until constant weight was achieved.

Several uranium peroxide samples were ignited at 850° for intervals totaling 80 h. The percentage of uranium continued to increase and, after the last ignition, was approximately 0.01% greater than the theoretical value, as shown in Fig. 1.

TABLE III

URANIUM CONTENT OF $U_3O_8$ PREPARED FROM URANIUM PEROXIDE IGNITED FOR 16 h AT 850°

| *Sample No.* | *Uranium (wt.%)* |
|---|---|
| 1 | 84.794 |
| 2 | 84.805 |
| 3 | 84.802 |
| 4 | 84.797 |
| Mean | 84.800 |
| Percent of theoretical value | 100.00 |

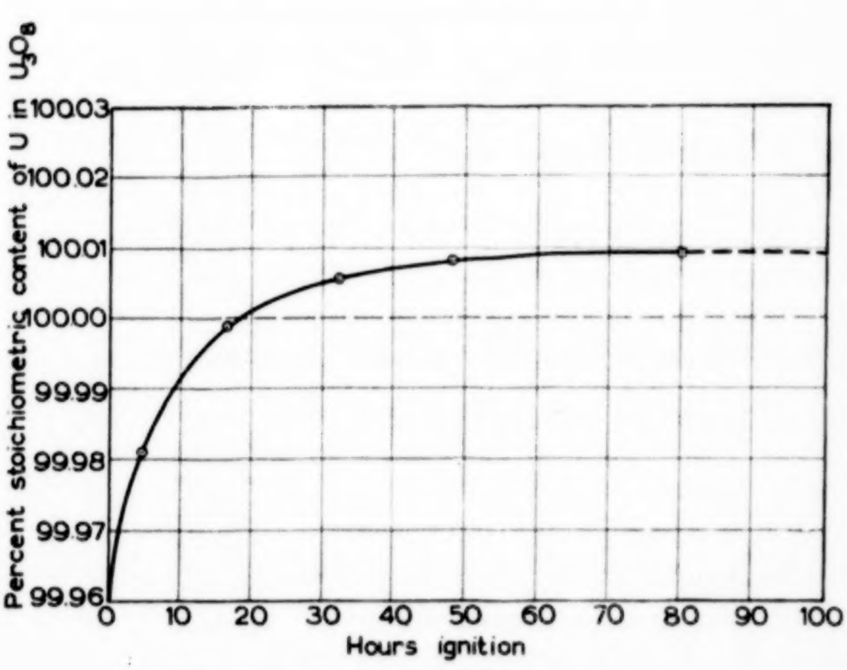

Fig. 1. $UO_4$ ignited to $U_3O_8$ at 850°.

To observe the effect, if any, of a low initial ignition temperature, 80 g of uranium peroxide was divided into two groups of four samples each. Group "A" was ignited at an initial temperature of 750° for two 2-h periods and then at 850° for 28 additional hours, for a total of 32 h. The other group, "B", was ignited at 850° for a total of 32 h. The uranium content of group "A" after the 32 h of ignition was approximately 99.96% of the theoretical value whereas group "B" was slightly greater than the theoretical value, making a difference in the uranium composition of the oxides of approximately 0.04% as shown in Fig. 2. This difference in uranium content indicates that the initial ignition temperature has some effect on the oxide composition.

The uranium peroxide for 14 uranium isotopic standards, each 1 kg of uranium, was converted to $U_3O_8$ in portions weighing 200–300 g by ignition at 850° for 32 h. The average uranium content of the oxide was 99.98 ± 0.01% of the expected theoretical value, indicating a probable influence of sample size upon the ignition time.

### *Uranium trioxide*

Samples of yellow uranium trioxide[7] were ignited at 850° for 16 h, and the oxide contained 84.770% uranium or 99.965% of the theoretical value as shown in Table IV.

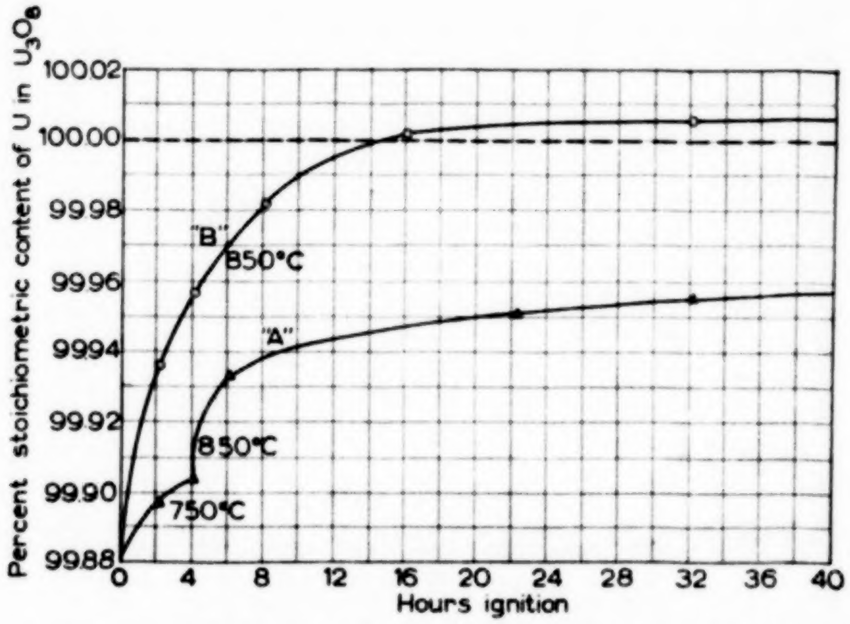

Fig. 2. Temperature effect of initial ignition of $UO_4$. $UO_4$ sample: Part (A) Ignition started at 750°; Part (B) Ignition started at 850°.

Samples of uranium trioxide, after conversion to $U_3O_8$, were ignited for 80 h at 850° and there was a gradual loss of oxygen with a corresponding increase in the uranium content; however, theoretical $U_3O_8$ was not obtained.

Samples of yellow uranium trioxide were ignited for 40 h at 900°, and the uranium content of the $U_3O_8$ was 99.99% of the theoretical value. Stoichiometric $U_3O_8$ was obtained after approximately 80 h of ignition, and 100.01% of the theoretical value was obtained after 140 h of ignition as shown in Fig. 3.

TABLE IV

URANIUM IN $U_3O_8$ FROM URANIUM TRIOXIDE IGNITED FOR 16 h AT 850°

| *Sample No.* | *Uranium (wt.%)* |
|---|---|
| 1 | 84.772 |
| 2 | 84.773 |
| 3 | 84.760 |
| 4 | 84.775 |
| Mean | 84.770 |
| Percent of theoretical value | 99.965 |

Stoichiometric $U_3O_8$ was produced by ignition of samples at 1000° for about 8 h, but these ignition conditions are so critical that slight variation in the temperature and/or period of ignition may vary the composition of the oxide significantly. The preferred procedure is to ignite for 16 h at 1000° and then at 850° for 2-h periods (usually two) until the weight becomes constant.

Uranium trioxide prepared for the production of uranium hexafluoride may contain 2000–3000 p.p.m. of sulphur to increase the reactivity during the reduction and fluorination processes. The $U_3O_8$ obtained by ignition of this uranium trioxide had a lower uranium content than that prepared from sulphur-free uranium trioxide ignited under identical conditions; however, the trace amount of sulphur that remained in the $U_3O_8$ did not account for this deficiency in the uranium content. Samples containing sulphur, when dissolved in hydrofluoric acid, dried under an infrared lamp, and ignited in a steam atmosphere for 2 h, produced an oxide that was similar in uranium content to that of a sulphur-free trioxide sample, as shown in Table V.

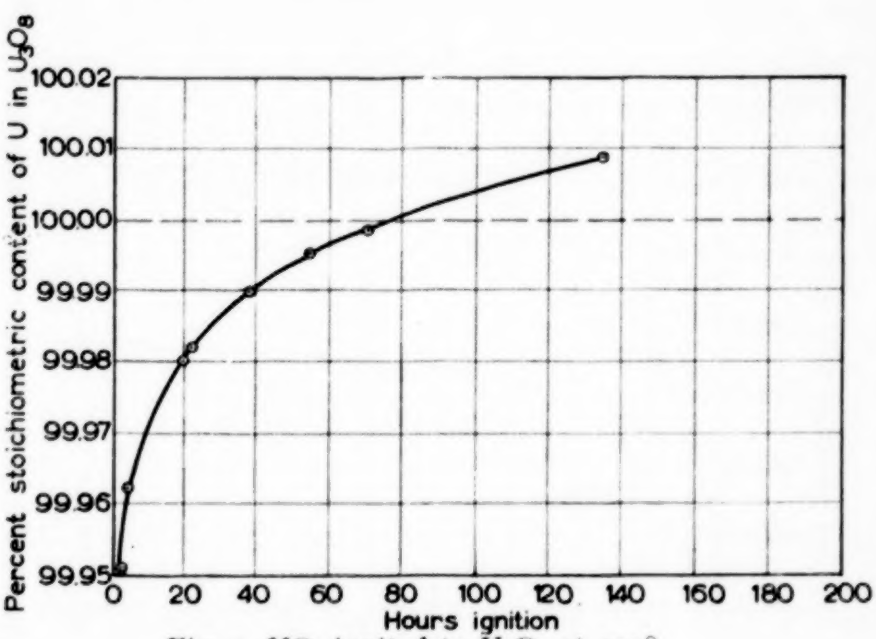

Fig. 3. $UO_3$ ignited to $U_3O_8$ at 900°.

TABLE V

URANIUM IN $U_3O_8$ FROM YELLOW URANIUM TRIOXIDE

All samples were ignited 2 h at 850° (steam atmosphere)

| *Type of sample* | *Uranium (wt.%)* |
|---|---|
| $UO_3$ containing sulphur | 84.698 |
| $UO_3$ containing sulphur and treated with HF | 84.767 |
| $UO_3$ without sulphur | 84.770 |

### *Uranyl nitrate*

Samples of uranyl nitrate were ignited for 100 h at 850° and the oxide produced was not stoichiometric; the uranium content of this oxide was 84.774%. Other uranyl nitrate samples were ignited for 2 h at 850° and for 16 h at 1000°, followed by a 2-h ignition at 850° before titration of the uranium. The average uranium content after each ignition is given in Table VI.

Samples of uranyl nitrate were ignited at 1000° for 28 h. The uranium content of the oxide was greater than the theoretical value and constant weight was not obtained.

### *Addition of hydrofluoric acid*

A stoichiometric oxide was formed when either uranyl nitrate or uranium trioxide was treated with concentrated hydrofluoric acid, evaporated to dryness, and ignited for 16 h at 850° (the first hour in a steam atmosphere).

TABLE VI

IGNITION OF URANYL NITRATE TO $U_3O_8$

| *Cumulative ignition conditions* | *Uranium (wt.%)* | *Theoretical value (%)* |
|---|---|---|
| 2 h at 850° | 84.765 | 99.959 |
| 16 h at 1000° | 84.818 | 100.021 |
| 2 h at 850° | 84.804 | 100.004 |

## DISCUSSION

Oxides which have been ignited for several hours at 850°, when ignited at 900° for 2 h, lose oxygen and show a change of about 0.01 to 0.02% in the oxide composition (Fig. 4). Oxides ignited for several hours at 850°, when ignited at 1000° for 2 h, lose oxygen and show an apparent increase of about 0.04 to 0.05% in the uranium content of the oxide. Thus, a change in the temperature of ignition varies the composition of the oxide.

Ignition of any of the parent materials at 1000° for many hours produces an oxide in which the uranium content is greater than that in stoichiometric $U_3O_8$, which is in disagreement with the findings of BROUNS AND MILLS who stated that under these ignition conditions constant weight and stoichiometric $U_3O_8$ are attained. The composition of this oxide changes little during storage but gains weight when ignited

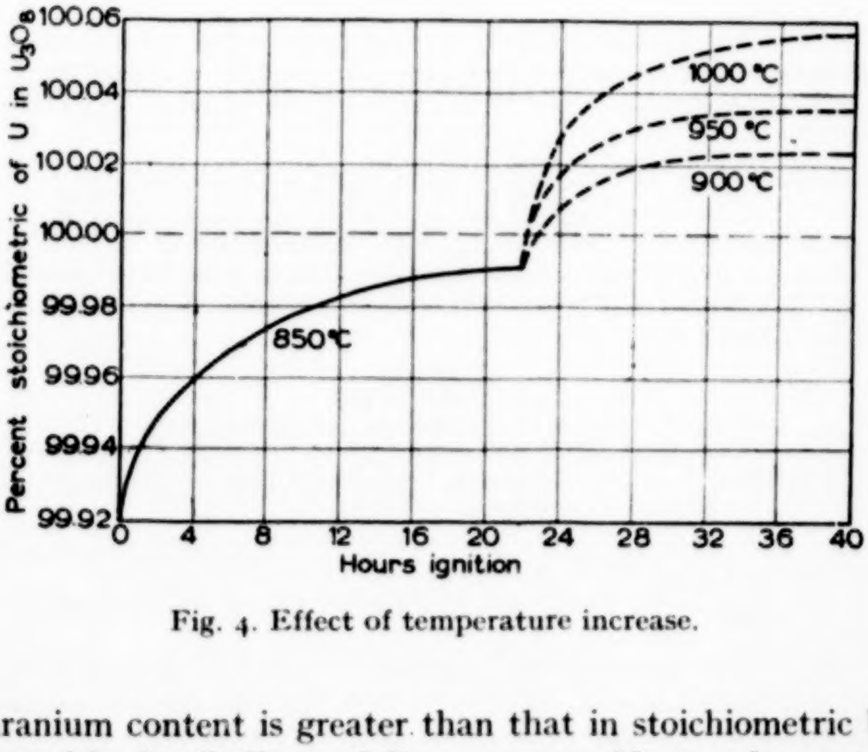

Fig. 4. Effect of temperature increase.

at 850° and again approaches the theoretical value after several hours of ignition at temperature.

During storage in unsealed plastic vials, $U_3O_8$ gains weight, which in turn lowers the uranium content of the oxide. This $U_3O_8$ will lose only a portion of this increase in weight when heated at 110° but will again approach the theoretical value upon ignition at 850°.

For most analytical work the use of a long ignition period is not practical; however, for analysis such as the determination of uranium in uranium trioxide by ignition, it is not necessary to ignite the sample for 80 h at 900° to obtain stoichiometric $U_3O_8$ for an accurate determination of the uranium content. Studies have shown that under controlled ignition conditions a constant value for the uranium in the oxide can be obtained from parent materials with the same chemical history of preparation. When the uranium content of the oxide, which is formed under rigidly controlled conditions of ignition, has been established by precise potentiometric titration, the resultant gravimetric factor can be applied in routine analytical procedures for the determination of uranium by direct ignition. The ignition time and temperature should be carefully controlled and periodic checks should be made to determine any variation in the gravimetric factor.

## SUMMARY

The preparation of stoichiometric $U_3O_8$ depends on the starting uranium compound, sample size, temperature, duration of ignition, and chemical alteration of the starting compound. Stoichiometric $U_3O_8$ was prepared in 10-g quantities from uranyl fluoride and uranium peroxide by ignition at 850° for 16 h, and from uranyl nitrate and uranium trioxide by ignition at 1000° for 16 h followed by re-ignition at 850° to constant weight. The ignition time required to produce a stoichiometric $U_3O_8$ may be decreased for many compounds by (*1*) converting the starting compound to uranium peroxide, or (*2*) treating the sample with hydrofluoric acid before ignition at 850° for 16 h.

## RÉSUMÉ

L'oxyde $U_3O_8$, de composition stoechiométrique, a été préparé par calcination à 850° de fluorure d'uranyle et de peroxyde d'uranium et par calcination à 1000° de nitrate d'uranyle et de trioxyde d'uranium, puis à 850° jusqu'à poids constant. Les auteurs ont examiné les possibilités de diminuer le temps de calcination.

## ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Darstellung von stöchiometrisch zusammengesetztem $U_3O_8$ aus Uranylfluorid und Uranylperoxyd durch längeres Erhitzen auf 850° oder aus Uranylnitrat und Urantrioxyd durch Erhitzen auf 1000° während 16 Stunden. Möglichkeiten zur Verkürzung der Glühdauer werden angegeben.

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# THE DETERMINATION OF URANIUM IN FAIRLY PURE BERYLLIUM METAL BY NEUTRON ACTIVATION AND GAMMA SPECTROMETRY

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(Received April 19th, 1961)

## INTRODUCTION

A simple and rapid method for the determination of trace quantities of uranium in a large number of beryllium metal samples was required. A neutron activation method in which the activated uranium could be measured directly on a single or multi-channel $\gamma$-spectrometer, without any radiochemical separations, answered these requirements. Because of the very low cross section (0.01 barns) for the $(n,\gamma)$ reaction on beryllium, and because of the extremely long half-life of the product of such a reaction ($> 10^6\ y$) the radioactivity formed during an irradiation of a few hours or days will be entirely due to impurities present in the beryllium. Provided that the photo-peak used to measure the uranium present can be identified and characterised precisely, any other radioactivity present in the sample will not cause interference. It is necessary, therefore, to establish the precise conditions of activation and measurement, paying particular attention to the instrumentation used in the counting.

## NUCLEAR CONSIDERATIONS

### *Data*

The nuclear characteristics of uranium and beryllium are shown in Table I. It should be noted that neptunium is formed as follows:

$$^{238}\text{U}\ (n,\gamma)\ ^{239}\text{U} \xrightarrow{\beta^-} {}^{239}\text{Np}$$

TABLE I

NUCLEAR DATA FOR BERYLLIUM AND URANIUM

| *Element* | *Nuclide* | *Abundance %* | *Cross section*[a] *(barns)* | *Radio-nuclide formed* | $T_{\frac{1}{2}}$ | *Max. β's (MeV)* | *γ's (MeV)* |
|---|---|---|---|---|---|---|---|
| Be | $^{9}$Be | 100 | 0.009 | $^{10}$Be | $2.7 \cdot 10^6$ yrs | — | — |
| U | $^{235}$U | 0.714 | 107 | $^{236}$U | $2.4 \cdot 10^7$ yrs | — | — |
|  | $^{235}$U | 0.714 | $\sigma_f = 582$ | Fission products | — | — | — |
|  | $^{238}$U | 99.3 | 2.74 | $^{239}$U | 23.5 min | 1.21 | 0.074 |
|  |  |  |  | $\beta^- \downarrow$ |  |  |  |
|  |  |  |  | $^{239}$Np | 2.3 days | 0.38 etc. | 0.106,<br>0.23 etc. |

[a] Activation cross section ($\sigma_{\text{act.}}$), except where fission cross section ($\sigma_f$).

Although the activation cross section for $^{238}$U is only 2.74 barns, the excitation function, showing the variation of total cross section with the energy of the incident neutron, as given by HUGHES AND SCHWARTZ[1], shows that at a neutron energy of 0.66 eV, $^{238}$U has a resonance peak of 72,000 barns, with other equally large resonances at higher neutron energies (2 to 100 eV). In addition to the predominant thermal flux of neutrons (0.0253 eV) in a nuclear reactor such as BEPO, there are also present intermediate energy and fast neutrons. The significance of these large resonances for $^{238}$U is discussed later.

### *Production of $^{239}U$ and $^{239}Np$*

The production of radioactive nuclides by irradiation in a neutron flux, can follow the scheme:

$$A \xrightarrow{(n,\gamma)} B \xrightarrow[\lambda_B]{\beta^-} C \xrightarrow[\lambda_C]{\beta^-} D \text{ (stable)} \tag{1}$$

where $A$ is the original stable species, $B$ is a radioactive species formed by neutron capture, $C$ is a radioactive species formed by $\beta^-$ decay, and $D$ is the stable product. After an irradiation time, $t$, the activities of $B$ and $C$, neglecting any $(n,\gamma)$ reactions directly on them, are given by $I_B$ and $I_C$, in disintegrations/unit time, respectively:

$$I_B = f\sigma_{\text{act.}}\, N_A(1 - e^{\lambda_B t}) \tag{2}$$

$$I_C = f\sigma_{\text{act.}}\, N_A \left[1 + \frac{\lambda_C}{\lambda_B - \lambda_C}\, e^{-\lambda_B t} - \frac{\lambda_B}{\lambda_B - \lambda_C}\, e^{-\lambda_C t}\right] \tag{3}$$

where $f\sigma_{\text{act.}} N_A$ is here the rate of production of $B$, $f$ = flux of neutrons, $N_A$ = original number of atoms of $A$, $\lambda_B$ = decay constant of radioactive species $B$, $\lambda_C$ = decay constant of radioactive species $C$, $t$ = time of irradiation and $\sigma_{\text{act.}}$ = activation cross section for $A$.

The formation of $^{239}$U and $^{239}$Np follows the general scheme:

$$^{238}\text{U} \xrightarrow{(n,\gamma)} {}^{239}\text{U} \xrightarrow[\text{23.5 min}]{\beta^-} {}^{239}\text{Np} \xrightarrow[\text{2.33 days}]{\beta^-} {}^{239}\text{Pu} \xrightarrow[\text{24,400 yrs.}]{\alpha} \tag{4}$$

and $^{239}$Pu may here be regarded as the stable product $D$, in eqn. (1). Writing the activities of $^{239}$U and $^{239}$Np as $I_B$ and $I_C$ respectively, and noting that

$$\lambda = \frac{0.693}{T_{\frac{1}{2}}} \tag{5}$$

where $T_{\frac{1}{2}}$ = the half-life of a radioactive species, and $\lambda$ = the decay constant of the radioactive species, we obtain, after simplification, the equations:

$$I_B = f\sigma_{\text{act.}}\, N_A(1 - e^{-0.03t}) \tag{6}$$

$$I_C = f\sigma_{\text{act.}}[1 + 0.0069\, e^{-0.03t} - 1.0068\, e^{-0.0002t}] \tag{7}$$

where again, $N_A$ = original number of $^{238}$U atoms, $f$ = neutron flux, $\sigma_{\text{act.}}$ = activation cross section for $^{238}$U, and $t$ = time of irradiation.

Fig. 1 shows eqns. (6) and (7) plotted to illustrate the growth of $^{239}$U and $^{239}$Np activities as functions of the irradiation time. The factor ($f\sigma_{act.}\ N_A$) is the saturation activity of $^{239}$U, (see eqn. (6)), and the ordinate represents the activities formed in terms of ($f\sigma_{act.}\ N_A$) taken as unity.

It is convenient to irradiate for $1\frac{1}{2}$ to 2 h, and it can be easily calculated that 1 μg of uranium will produce at the end of a 100-min irradiation, $4.0 \cdot 10^5$ dis/min. The $^{239}$Np activity accumulated in this time is $8 \cdot 10^3$ dis/min (Fig. 1). If the uranium is now allowed to stand for 1,000 min (17 h approximately) the activity of $^{239}$U is zero, and that due to the $^{239}$Np is then $8.2 \cdot 10^3$ dis/min.

### *Fission of $^{235}$U*

The $^{235}$U present in natural uranium undergoes fission on slow neutron irradiation, and it has been shown by SMALES[2], that 12.8-day $^{140}$Ba, one of the fission products formed, can be used to determine the uranium content. This method, of course, requires careful radiochemical separations, and this precludes its use in direct γ-spectrometry. It might be possible to use another fission product of suitable half-life, decay scheme and fission yield, but for natural uranium any single fission-product, to be preferable to $^{239}$U or $^{239}$Np, must overcome an initial handicap of having a fission yield value which cannot be more than about 0.06.

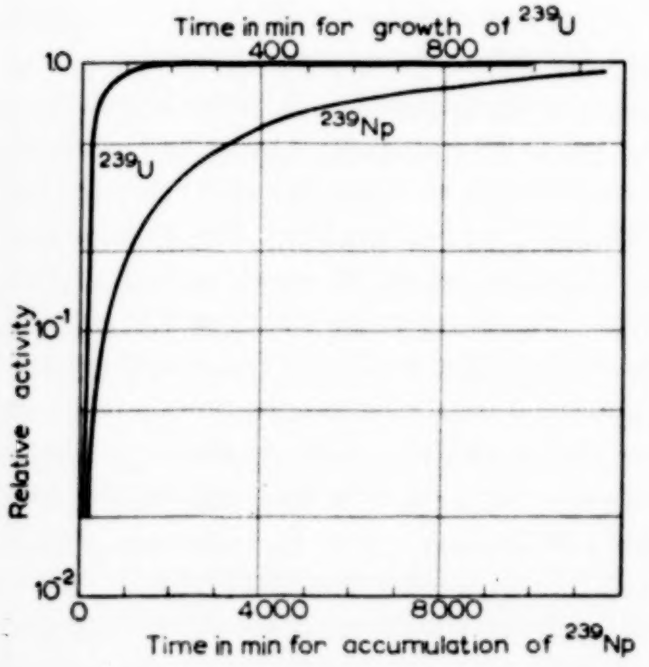

Fig. 1. Growth of $^{239}$U and $^{239}$Np in terms of "saturation activity" ($f\sigma_{act.}\ N_A$), of the nuclear reaction, $^{238}\text{U}\ (n,\gamma)\ ^{239}\text{U} \xrightarrow{\beta^-} {}^{239}\text{Np}$.

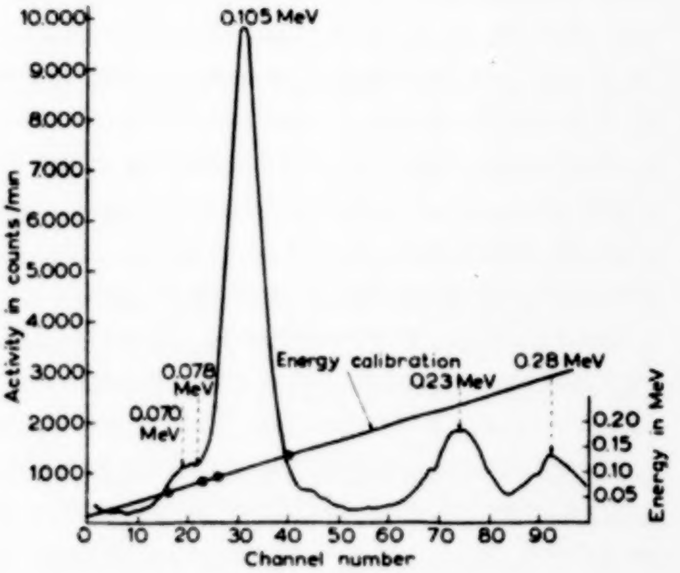

Fig. 2. Spectrum of $^{239}$Np obtained on 99-channel Philips 1438B analyser, using 3" × 3" NaI(Tl) crystal.

## γ-SPECTROMETRY

### *General features of method*

The instrumentation used and the theoretical considerations involved in γ-spectrometry have been described elsewhere[3]. The advantages of a multi-channel analyser are numerous, and this instrument has played an important part in recent developments in activation analysis. It is particularly satisfactory for measuring low activities, say 100 $\gamma$-counts/min above background, enabling a considerable saving in time and an improvement in counting precision to be made compared with single-channel instruments. The main disadvantage is the high paralysis (or "dead") time, of 700 to 800 $\mu$sec, which restricts the total counting rates, if quantitative measurements are to be made.

Some preliminary work using a 3" × 3" NaI(Tl) crystal, in conjunction with a Philips 1438B, 99-channel analyser (Wilkinson type), indicated that sample weights of 50 mg or less of beryllium metal would be necessary, if the total $\gamma$-activity produced on irradiating the sample for 1½ h, followed by 24-h standing time, was not to interfere with the photo-peak being measured.

No particular advantage was found in the double-crystal type of spectrometer, which enables the Compton continuum to be subtracted; nor in the use of a wafer type NaI(Tl) crystal, for selectively measuring very low energy $\gamma$-photons in the presence of higher energy $\gamma$-emitters. The main disadvantage, at present, of the latter method is the poor resolution ($\not<$15%) of the thin crystals.

### *Description of instrument used*

The single-channel $\gamma$-spectrometer does not suffer from paralysis difficulties, since the overall resolving time can be made as low as 5 $\mu$sec. Since the spectra are normally recorded on a chart-recorder, this instrument offers a convenient method for the routine analysis of many samples.

The instrumentation used in the present work consisted of a 1" × 1½" NaI(Tl) crystal mounted on an E.M.I. 6097 photomultiplier tube, whose operating voltage was supplied by an E.H.T. unit. The output pulses were amplified via a cathode follower, by a non-overloading linear amplifier, and passed to an analyser. The pulses selected by the single channel voltage discriminator, were fed to a ratemeter and recorded on a chart-recorder. The discriminator is swept across the spectrum by a scanning potentiometer, connected to the paper drive. The channel width, as determined with a pulse-generator was 2 ± 0.04 V. The samples were normally counted by placing them directly on the aluminium cover of the crystal for a 30 min scanning period.

In addition, a 100-channel, Type 1363B analyser (Hutchinson-Scarrott), with an oscilloscope display, was also connected to the amplifier. This enabled a visual examination of the spectrum to be made, after only 1 or 2 min of counting. In this way contaminating $\gamma$-emitters could be readily discerned.

The use of the Nuclear Enterprises (G.B.) Ltd. non-overloading linear pulse amplifier, NE. 5202, described by FAIRSTEIN[4], ensured that even total counting rates of 100,000 counts/min, (when the irradiated sample was placed on the crystal), could be dealt with satisfactorily. It was established that using an ordinary linear amplifier, pulse distortion occurred in the channels used to record low $\gamma$-energies, by contributions from the high (>0.2 MeV) $\gamma$-emitters in the sample. This would lead to incorrect counting rates being recorded under a particular photo-peak.

The 1" × 1½" NaI(Tl) crystal was shielded by a 1½" lead castle, of external dimensions 6½" × 6½", so that the crystal was 3" below the lead. When $\gamma$-rays undergo Compton degradation in the shielding material, they will produce back-scattered radiation which is detected photoelectrically by the crystal. The *ideal* shielding arrangement to minimise this effect should, as indicated by HEATH[5], give as great a linear distance as possible between the crystal and the shielding material.

A further effect of the absorption of low energy radiation in the shielding is the production of Pb X-rays of 75.1 keV. In order to eliminate this, a liner of cadmium foil, 0.040″ thick, was used, as this has a high absorption cross-section for the lead fluorescent radiation.

## EXPERIMENTAL

### *Measurement of $^{239}U$*

Since $^{239}$U has a half-life of 23 min, it must be counted as soon as possible. An irradiated beryllium sample was counted on the single-channel $\gamma$-spectrometer, immediately after irradiation. The photo-peak produced by the 74 keV (0.074 MeV) $\gamma$-photon of $^{239}$U was measured, over a period of 3 h. The decay curve was plotted, and the presence of longer-lived $\gamma$-impurities was evident. All the beryllium samples examined showed the presence of impurities at this energy, and it was clear that no accurate uranium results could be obtained by a single measurement of the 74 keV photo-peak. The $^{239}$U results are discussed below. Since the plotting of decay curves would considerably increase the time required in the determination, the use of $^{239}$U was inadvisable.

### *Choice of $^{239}Np$*

After allowing the irradiated beryllium samples to "cool" for about 24 h, a considerable amount of the shorter lived $\gamma$-emitting impurities had decayed. Although the sensitivity of the method, as shown above, is considerably less for $^{239}$Np than $^{239}$U, at the 10 p.p.m. level on 0.3- to 0.5-g samples of beryllium, $^{239}$Np photo-peaks were easily detectable above the general activity produced in the irradiated samples. In addition, the longer half-life of 2.33 days, enabled a routine method to be more easily used.

A consideration of the decay scheme[6] of 2.33-day $^{239}$Np shows that a number of $\gamma$-photons are emitted, most of which undergo electron conversion. From the data supplied, it is seen that the most important $\gamma$-photons have energies of 0.106, 0.23, 0.28 MeV respectively, the 0.106 MeV $\gamma$-photon being predominant. In addition 34.2% of all the $\gamma$-photons emitted result from the production of the $K$ X-rays of $^{239}$Pu, which have energies of 98 to 106 keV. These contribute approximately 48% of the $\gamma$-photons measured in the 100 keV region for $^{239}$Np.

The spectrum of $^{239}$Np measured on the Philips 99-channel instrument, using a 3″ × 3″ NaI(Tl) crystal, is shown in Fig. 2. This shows the predominant composite photo-peak at 0.105 MeV, with the minor subsidiary peaks at 0.23 and 0.28 MeV respectively. It will be observed that a minor peak appears on the low-energy side of the main photo-peak, in the region 0.070 to 0.078 MeV, and that it cannot be resolved from the main peak at 0.105 MeV. This "escape peak" is due to the loss of the iodine $K$ X-ray, produced by the photoelectric effect, from the crystal. It is only prominent for $\gamma$-energies in the region 32–100 keV, appearing at 28 keV less than the main peak, and is more pronounced the smaller the crystal[3]. Further, a maximum Compton energy photon at 75 keV will be produced by 0.106-MeV $\gamma$-photons, this also being more pronounced in small crystals. All the spectra recorded on the single-channel instrument showed this "subsidiary" peak at 70 to 80 keV.

Fig. 3a shows the $^{239}$Np spectrum from an irradiated beryllium sample, obtained on the 3″ × 3″ NaI(Tl) crystal and the Philips 99-channel analyser. Fig. 3b shows a similar spectrum recorded on the single-channel instrument, and Fig. 4 is the half-life of the photo-peak shown in Fig. 3a, plotted over 9 days (4 half-lives). The value obtained was 2.46 days compared with the reported 2.33 days. The exact characterisation of the $\gamma$-energy and half-life of the $^{239}$Np in this way indicates the specificity of the radio-nuclide for the determination of uranium.

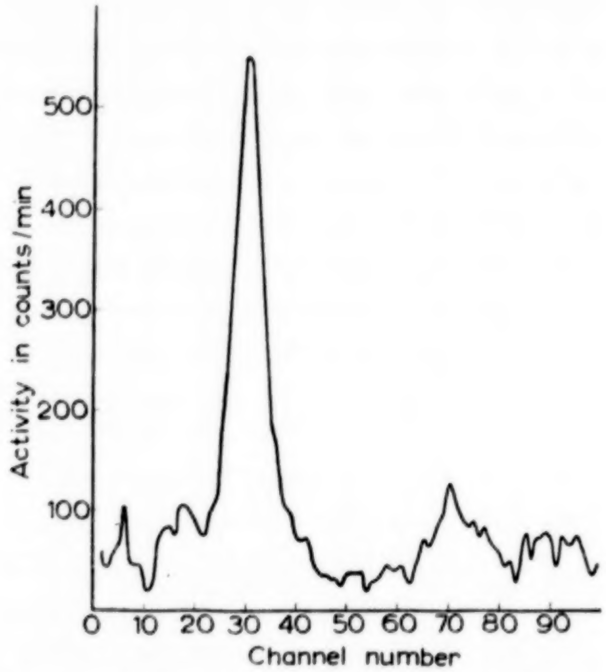

Fig. 3a. $^{239}$Np photo-peak from an irradiated sample of beryllium metal, obtained on 99-channel Philips analyser, using 3″ × 3″ NaI(Tl) crystal.

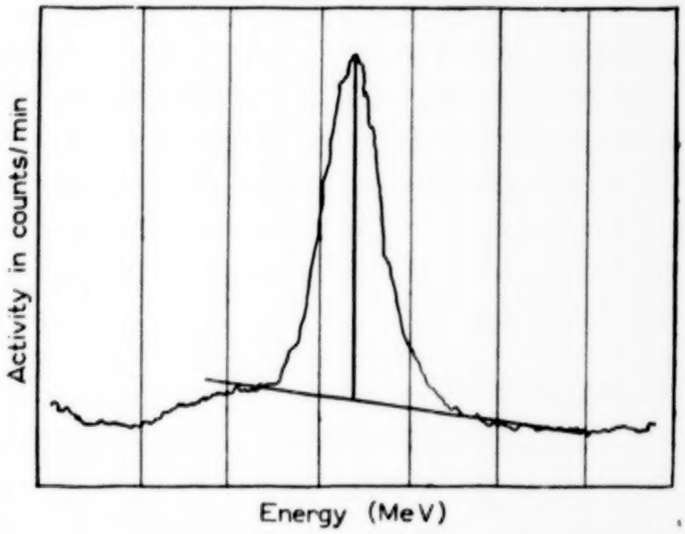

Fig. 3b. $^{239}$Np photo-peak from an irradiated sample of beryllium metal, obtained on single-channel $\gamma$-spectrometer, using 1″ × 1½″ NaI(Tl) crystal.

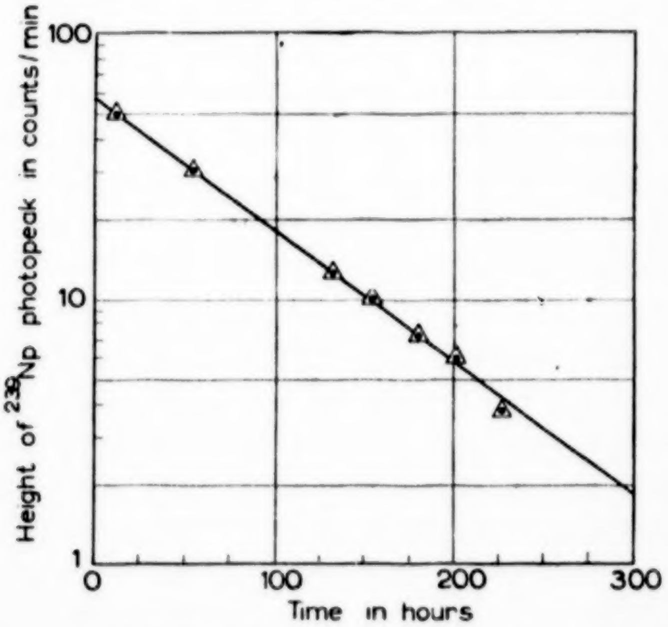

Fig. 4. Decay curve of $^{239}$Np photo-peak, measured on a beryllium sample.

### *Measurement of peak-heights*

The heights of the photo-peaks produced under identical conditions of counting, by both sample and standard, were compared. In practice, it was found satisfactory to use this parameter, rather than more involved methods of determining the counting rates under the full-energy photo-peak. A straight line was drawn joining the two valleys on either side of the photo-peak and the vertical distance between this base line and the top of the peak was measured. This is shown in Fig. 3b.

The precision of this method of measurement is well within the overall precision required, and simplifies the calculations involved.

### *Use of a cadmium box*

It was stated earlier that $^{238}$U has a resonance peak of 72,000 barns at a neutron energy of 0.66 eV. Cadmium foil 0.6 mm thick absorbs all thermal neutrons below 0.4 eV. It is possible, therefore, to irradiate selectively the sample inside a cadmium box, and to reduce the intensity of radioactivity produced by thermal neutron capture in the impurities in the beryllium, without seriously reducing the activity induced in the uranium.

When an experiment was made to test this, it was found that whereas the activity produced by the $^{239}$Np had been reduced by 19%, the total activity in a typical beryllium sample, was reduced by 43%. This was not a sufficient reduction in a total activity of 60 counts/min/mg of irradiated beryllium, to improve significantly the relative peak height of the $^{239}$Np measured above the general activity. As the use of large amounts of cadmium introduce irradiation difficulties, this method of selective irradiation was not applied.

### *Irradiation of beryllium samples and uranium standards*

As in all neutron activation work involving nuclear reactors, errors due to variations in pile flux, self-shielding in samples or standards etc., must be avoided. The samples were packed in polythene containers ("polytainers") which were cut to a depth of ½ inch and had ⅜ inch i.d., with a tight fitting press-on cap. Only five polytainers could be accommodated in a standard 3" aluminium irradiation can, together with two sealed thin walled silica ampoules, containing 0.1 ml of the standard uranium solution, (50 $\mu$g U/ml). None of these materials, nor the beryllium samples, would produce self-shielding difficulties.

It is known that no flux variation occurs in the vicinity of the position in BEPO used for the irradiation, and the fact that the samples were distributed along the axis of the can introduced no errors.

Five samples and two standards were always irradiated together. This arrangement enabled the analysis of a large number of samples to be carried out smoothly. A 1- to 1½-h irradiation followed by 1 to 2 days cooling, making this procedure practicable.

### *Treatment of samples and standards after irradiation*

For irradiations of 1 to 1½ h ,followed by 1 to 2 days cooling, the activity produced in the polytainer was negligible compared with the overall activity of the beryllium sample. This meant that there was no need to transfer the sample to a new polytainer, prior to its being counted.

The standards, after irradiation, were quantitatively transferred to precisely similar polytainers as used for the samples, and the volume made up with water, to that occupied by the samples. By counting the sample and standard polytainers at a fixed position on the crystal, geometry errors in counting were avoided. In addition, the attenuation of $\gamma$-rays in the light elements, Be, H and O is closely comparable.

## NUCLEAR LIMITATION CONSIDERATIONS

### $(\gamma,n)$ *reaction on beryllium*

The possibility that beryllium will undergo the reaction:

$$^{9}\mathrm{Be}\,(\gamma,n)\,^{8}\mathrm{Be} \rightarrow 2\,^{4}\mathrm{He}$$

and hence produce an enhanced neutron flux in the beryllium samples was considered. The threshold for this reaction[7] is 1.665 MeV. No precise information on the energy distribution of the $\gamma$-flux in the reactor is available, except that in the position where the irradiations were carried out in BEPO, the $\gamma$-rays would produce a radiation dose equivalent to $1.8 \cdot 10^{6}$ R/h. On irradiating beryllium samples containing $< 1$ p.p.m. U, "spiked" with 5- to 10-$\mu g$ amounts of uranium, together with pure uranium standards, no evidence of enhancement of the neutron flux was obtained.

### *Production of "spurious"* $^{239}Np$

There are no naturally occurring elements, which on neutron irradiation in a nuclear reactor, could undergo, $(n,p)$, $(n,\alpha)$ or $(\gamma,n)$ reactions that could produce $^{239}$Np. In this respect the use of $^{239}$Np (or $^{239}$U) is quite specific for the determination of uranium by neutron activation.

### *Effect of isotopic composition of uranium*

The activation method described here measures, strictly speaking, only the $^{238}$U isotope, and can only give the total uranium content if an isotopic abundance measurement, usually but not exclusively made by mass spectrometry, confirms that the uranium in the sample is essentially all $^{238}$U. The standards contain natural uranium *i.e.* 99.3% $^{238}$U, 0.7% $^{235}$U.

Of course, slight enrichment or depletion of the $^{235}$U isotope in the sample will not seriously affect the $^{238}$U proportion, and therefore the method can be applied with reasonable accuracy to such samples.

If, however, the interest is not in the total uranium, nor the $^{238}$U, but in the $^{235}$U, and for some nuclear energy purposes this may well be the case, then the method described can *not* be assumed to give accurate results unless supported by additional information on the isotopic composition of the uranium in the sample. Such information might be obtained by mass spectrometry or by neutron activation of $^{235}$U, *e.g.* SEYFANG AND SMALES[8], MAY AND LÉVÊQUE[9], and HERR AND MERZ[10].

## METHOD

### *Preparation of samples and standards for irradiation*

Cut a ⅜" i.d. polythene container, ("polytainer"), to approximately ½" in length, and refit the polythene cap. Number the container and weigh it accurately. Introduce the beryllium metal until the container is full to ⅛" from the top, and after refitting the polythene cap, re-weigh. By means of a hot air jet, heat-seal the cap. Carefully pack the prepared samples into the standard 3" × 1" aluminium irradiation can, using aluminium foil or silica wool as a packing material. Only five prepared polytainers can be packed into a single can.

Prepare two silica ampoules, sealed at one end, and having two constrictions along their length. Using a micro-dropping pipette ("spitzer") introduce approximately 0.1 ml of a standard uranium solution (50 $\mu g$ U/ml) into the weighed ampoules, re-weigh the ampoules and then seal them, using the top constrictions. The two standard ampoules are wrapped in aluminium foil and packed carefully alongside the samples in the irradiation can. Each can used for an irradiation must possess its own standards. The aluminium irradiation can is irradiated in the appropriate manner, in a nuclear reactor, at a flux of $10^{12}$ neutrons/cm$^2$/sec, for 1 to 1½ h. Allow the irradiation can (shielded behind lead) to cool for 24 to 48 h, from the end of the irradiation.

### *Preparation of standards after irradiation*

Unpack the samples and standards, observing the usual precautions. Spin one of the silica ampoules in a centrifuge and break it open at the constriction. Now transfer quantitatively the solution, using a "spitzer", to a similar polytainer, as used for the samples. Wash the ampoule with a small amount of water, transferring the washings in a similar manner. Adjust the height of the solution in the polytainer so that it is equal to the height of the beryllium in the sample container. Replace the cap firmly, making certain the outside of the polytainer is wiped clean.

### *Counting of samples and standards*

Set up the single-channel $\gamma$-spectrometer, so that the channel width is about 2 V, and connect the instrument to a pen-recorder with a scanning potentiometer ganged to a paper drive. Choose the settings of gain on the amplifier, and of range and integrating capacity on the ratemeter so that the spectrum scanned is over the appropriate range of $\gamma$-energies to be measured. The standard sample can be used to find appropriate settings. Also, standard $\gamma$-energy sources, such as 0.084 MeV $^{170}$Tm and 0.134 MeV $^{144}$Ce can be used for calibration purposes. Adjust the potentiometer setting on the chart-recorder for a scan-rate of 30 min.

Count both sample and standard separately under identical conditions, of geometry, instrumental settings, etc. The recorder can be adjusted so that only the 0.106 MeV peak of $^{239}$Np and its adjacent background, is actually scanned. This need only take 10–15 min. Provided that all the samples and standards are counted in a short period (1–2 h) decay corrections are unnecessary.

Check that the photo-peak of the sample is identical with that produced by the standard, and that no contaminating peaks are causing interference. Choose one sample and a standard for decay measurements extending over 8 to 10 days, for confirmation of the half-life.

### *Calculations*

Draw a straight line from the valley on either side of the peak (see Fig. 3b), and measure the peak-height above this line. Do this for sample and standard. From the measured peak-heights for sample and standard, sample weight and amount of standard taken, calculate the amount of natural uranium in the sample in p.p.m.

## RESULTS AND DISCUSSION

### $^{239}$*U*, $^{239}$*Np and* $^{140}$*Ba results compared*

Six samples of beryllium metal were irradiated for 30 min together with uranium standard solutions, and the $^{239}$U content was measured immediately after the irradiation on the single-channel $\gamma$-spectrometer. The samples were counted 1 inch above the crystal, because of the gross $\gamma$-activity. The samples were again counted, this time on the surface of the crystal, 24 h later, and the $^{239}$Np photo-peak measured. The samples and standards were then ***re-irradiated*** for a further 3 days and allowed to cool. The beryllium was then dissolved in the presence of barium carrier, the barium radiochemically purified, and the uranium determined by counting the $^{140}$Ba, as described by SMALES[2]. A comparison of the results obtained is given in Table II, and since the three determinations were carried out on the *same* sample, errors due to inhomogeneity of the sample were avoided.

TABLE II

COMPARISON OF RESULTS OBTAINED BY $^{239}$U, $^{239}$Np AND $^{140}$Ba

| *Sample* | $^{239}$*U* (*p.p.m.*) | $^{239}$*Np* (*p.p.m.*) | $^{140}$*Ba* (*p.p.m.*) |
|---|---|---|---|
| A | 11.6 | 10.3 | 11.4 |
| B | 11.8 | 9.7 | 10.4 |
| C | 18.4 | 12.0 | 14.6 |
| D | 19.7 | 13.1 | 14.0 |
| E | 21.2 | 15.9 | 14.9 |
| F | 18.7 | 13.1 | 12.4 |

The results in Table II demonstrate (*a*) the high results obtained generally by the $^{239}$U method, (*b*) the satisfactory agreement, within the limits of precision of the $^{239}$Np method, between the $^{239}$Np and $^{140}$Ba results. The latter agreement suggests also that the isotopic composition of the uranium in the samples was not widely different from natural.

TABLE III

REPRODUCIBILITY OF $^{239}$Np MEASUREMENTS

Sample G containing 10.2 p.p.m. U

| *Portion* | *Peak-height/g Be* |
|---|---|
| I | 157 units |
| II | 149 units |
| III | 148 units |
| IV | 152 units |
| V | 146 units |
| | Average = 150 |
| | $\sigma = \pm 4.3$ |
| | Coeff. of variation = ±2.9% |

### *Reproducibility of $^{239}$Np measurements*

The reproducibility of the method was examined by the following experiment. A uniform sample of beryllium metal was selected and divided into five portions. These were then irradiated, with uranium standards, in the usual way and the $^{239}$Np measured on the single-channel $\gamma$-spectrometer 24 h later. The results obtained, expressed in arbitrary peak-height units, are given in Table III.

### *Conclusion*

The method described in this paper enabled nearly 200 samples of beryllium to be analysed for their uranium content in about 14 days by one operator. The advantages of the $^{239}$Np method have been stressed, and for samples of beryllium containing $>1$ p.p.m. U, the sensitivity is satisfactory. When samples containing $<1$ p.p.m. U are to be analysed, the $^{140}$Ba method, involving chemical separation, is the most sensitive. However, for samples of beryllium metal with a greater degree of purity than those encountered in the present work, direct $\gamma$-spectrometric methods may still have certain advantages.

The method is not subject to any severe nuclear limitations and possesses reasonable accuracy, provided that the isotopic composition of the uranium is normal. The precision of the method is within $\pm 10\%$.

## ACKNOWLEDGEMENTS

The authors wish to thank particularly MR. J. COLMAR, Production Group, U.K.A.E.A., Springfields, Lancs. for his sustained effort in carrying out the many analyses required. One of us (A.P.S.) was temporarily transferred to Harwell from Springfields, for some of this work, and we would like to thank Mr. T. G. CLINTON, General Manager, Chemical and Metallurgical Services Department, U.K.A.E.A., Springfields, Lancashire, for giving his permission for that transfer.

## SUMMARY

A method is described for the determination of trace quantities of uranium in beryllium metal. The beryllium samples are irradiated in "polytainers" for 1½ to 2 h in a flux of $10^{12}$ neutrons/cm$^2$/sec (as in BEPO), allowed to stand for 24 h, then measured directly without any further treatment on a $\gamma$-spectrometer. The radio-nuclide used is 2.33-day $^{239}$Np, which produces a satisfactory photo-peak with a 1" × 1½" NaI(Tl) crystal and single-channel $\gamma$-spectrometer. Dilute solutions (50 $\mu$g/ml) of uranium are used as standards, and after irradiation, prepared in similar polytainers as used for the samples. As little as 1 p.p.m. of uranium can be determined in 0.5-g samples of beryllium metal; for greater sensitivity radio-chemical separations would be required. Much of the radioactivity produced in the sample is due to the impurities it contains, and it is this radioactivity which limits the sensitivity of the direct $\gamma$-spectrometric method. Full details of the method are given, and various factors which may be a source of error are discussed.

## RÉSUMÉ

Une méthode radiochimique est décrite pour le dosage de traces d'uranium dans le béryllium. On procède par activation au moyen de neutrons et spectrométrie gamma. Il est possible de doser ainsi 1 p.p.m. d'uranium dans des échantillons de béryllium de 0.5 g.

## ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Uran in Beryllium durch Aktivierung mit Neutronen und Gammaspektrometrie.

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## Short Communication

# A solvent extraction system for 2,4-dinitrophenylhydrazones
# Application to the hydrazones of oxidation products of β-alanine and hydrolyzed calcium *d*-pantothenate

In studies on methods for the determination of calcium pantothenate, a hydrolytic product, β-alanine, was tested with 2,4-dinitrophenylhydrazine according to the method of SZALKOWSKI, MADER AND FREDIANI[1]. However, the hydrazone was not obtained in a high enough yield to be used as an estimate of the amino acid at low concentrations. A solvent extraction system was developed which eliminated precipitation, washing, drying, and dissolution of the hydrazone formed after the reaction. The amount of hydrazone in the resulting extract could be read directly in a spectrophotometer with approximately 10 times greater sensitivity than in the original method. This system might be of interest to analysts engaged in the quantitative measurement of hydrazones.

The procedures for oxidation, hydrazone formation and extraction are as follows. To a 5-ml solution of β-alanine in a 40-ml glass-stoppered centrifuge tube add 2 ml of 1:1 sulfuric acid, 1 ml of 12% potassium bromide, and 3 ml of 4% potassium permanganate solutions. Stopper, mix and let stand at room temperature for 10 min. Transfer to an ice-bath for 5 min, add dropwise 10% aqueous sodium sulfite solution until the solution turns colorless, then add 1 ml of a 1% solution of 2,4-dinitrophenylhydrazine in 3 *N* hydrochloric acid and autoclave the contents of the tube at 15 p.s.i. for 30 min. After cooling to room temperature, add 7 ml of benzyl alcohol, shake for 10 min, centrifuge at 1000 r.p.m. for 5 min and discard the aqueous layer. To the benzyl alcohol solution add 1 to 2 g of anhydrous sodium sulfate, and after centrifugation, transfer a 5-ml aliquot to another centrifuge tube, and add 20 ml of carbon tetrachloride and 10 ml of 1:4 ethanol–1 *N* sodium hydroxide solution. Stopper, shake for 5 min and centrifuge. Siphon off the blue aqueous layer and read at 570 mμ in a spectrophotometer. It was found that the reaction was quantitative, and followed the Beer-Lambert law for amounts of β-alanine up to 20 μg.

In applying the above reactions to the determination of calcium *d*-pantothenate, the following method was employed. Chromatograph 5 ml of the solution of the vitamin on a 5 × 50 mm column (in a tube with a reservoir of about 10-ml capacity) of Amberlite CG-400, type I, which had been saturated with 5% boric acid solution. Wash the column twice with 5 ml of 5% boric acid, once with 5 ml of water, and discard the washings. Elute the adsorbed pantothenate with 5 ml of borate–trichloroacetic acid solution (made by adding a 0.2 *M* solution of sodium tetraborate to 50 ml of 0.2 *M* trichloroacetic acid to give pH 7.1, and diluting to 100 ml). Hydrolyze the pantothenate in the effluent by adding 1 ml of 2 *N* hydrochloric acid, and autoclaving at 15 p.s.i. for 30 min. Cool to room temperature, and treat according to the above procedure, beginning with the addition of 2 ml of 1:1 sulfuric acid. A direct absorbance–concentration relationship was observed up to 100 μg of calcium *d*-pantothenate.

Reported interference of ascorbic acid[1] was not eliminated by the above chromatographic procedure. It was possible, however, to differentiate the hydrazone of ascorbic acid after oxidation from those of other keto compounds, by carrying out the reaction at lower temperatures[2]. α-Alanine did not react in this method. The high sensitivity of the method may be useful in the determination of calcium *d*-pantothenate in low concentrations which cannot be detected by other chemical methods, such as the 1,2-naphthoquinone-4-sulfonate procedure developed in this laboratory. Details of the latter method will be discussed in a later publication[3].

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[1] C. R. SZALKOWSKI, W. J. MADER AND H. A. FREDIANI, *Cereal Chem.*, 28 (1951) 218.
[2] J. H. ROE, *J. Biol. Chem.*, 236 (1961) 1611.
[3] T. PANALAKS AND J. A. CAMPBELL, *Anal. Chem.*, in the press.

Received July 28th, 1961

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## Publications received

1. Kjeller Research Establishment, *Quarterly Progress Report No. 1*, Institute for Atomic Energy, Lillestrøm, Norway, June 1961.
2. *Actas do Congresso, XV Congresso Internacional de Quimica Pura e Aplicada*, Lisboa, 8–16 de Setembro, 1956, Vol. III, Ramos, Afonso e Moita, Lisboa, 1961, 978 pp.
3. *Titrace v Nevodných Prostředich (Titrations in Non-aqueous Media), Moderni Metody v Chemické Laboratoři*, Svazek 3, J. Kucharsky and L. Šafařík, Státní Nakladatelství Technické Literatury, Praha 1961, 201 pp.

# Announcements

## INTERNATIONAL CONFERENCE ON SPECTROSCOPY, PRELIMINARY PROGRAM

The International Conference on Spectroscopy and Xth Colloquium Spectroscopicum Internationale will be held June 18–22, 1962, at the University of Maryland, College Park, Md., in suburban Washington, D.C. The Conference, being organized by the Society for Applied Spectroscopy with the aid of an International Advisory Board, will include a series of invited lectures on currently important themes in spectroscopy and also contributed papers related to these themes. Among the speakers will be:

Prof. J. L. GREENSTEIN (Pasadena): The Role of Spectroscopy in Astrophysics.
Dr. T. A. CHUBB (Washington): Measurement of Ultraviolet and X-Ray Radiation from above the Atmosphere.
Prof. H. KAISER (Dortmund): Critical Review of Methods and Results of Time-Resolved Spectroscopy.
Prof. C. T. J. ALKEMADE (Utrecht): Excitation and Related Phenomena in Flames.
Dr. A. WALSH (Melbourne): Atomic Absorption Spectroscopy.
Dr. L. BELLAMY (London): Factors influencing the Position of Group Frequencies in Infrared Spectra.
Prof. H. H. GÜNTHARD (Zurich): Interrelated Problems in Nuclear Magnetic Resonance and Molecular Spectroscopy.
Prof. J. H. JAFFE (Rehovoth): Spectral Line Shape and Molecular Interaction.
Dr. R. NORMAN JONES (Ottawa): Comparative Studies of Infrared and Raman Group Frequencies and their Applications.
Dr. A. J. AHEARN (Murray Hill): Vacuum Spark Mass Spectrographic Analysis of Solids.
Dr. J. BEYNON (Manchester): Correlation of Mass Spectra with Molecular Structure.
Prof. C. HUTCHINSON (Chicago): Electron Spin Resonance.
Prof. R. RICHARDS (Oxford): Applications of Nuclear Magnetic Resonance.
Dr. D. WHIFFEN (Teddington): Electron Spin Resonance and Free Radical Structure.
Dr. B. VODAR (Bellevue): Extreme Ultraviolet Spectra.
Dr. D. A. RAMSAY (Ottawa): Spectra of Gaseous Gree Radicals.
Dr. B. P. STOICHEFF (Ottawa): On the Application of Optical Masers to Spectroscopic Studies.
Dr. J. PHILIBERT (St. Germain-en-Laye) and Prof. V. E. COSLETT (Cambridge) Studies on X-Ray Spectra.

Authors desiring to submit a 20-min paper for inclusion in the full program of the meeting should forward a title, names of authors, and a 250- to 300-word abstract before December 31, 1961. This information, as well as requests for further details on the meeting, should be sent to BOURDON F. SCRIBNER, General Chairman, International Conference on Spectroscopy, 1962, National Bureau of Standards, Washington 25, D.C. (U.S.A.).

# FEIGL ANNIVERSARY SYMPOSIUM 1962

*Held in Honour of Professor F. Feigl to commemorate his 70th Birthday*

An International Symposium on Analytical Chemistry will be held in the University of Birmingham, Edgbaston, Birmingham 15, England during the period April 9 to 12, 1962, inclusive. The Symposium is organized by the Midlands Section of the Society for Analytical Chemistry under the patronage of the International Union of Pure and Applied Chemistry. The programme will consist of:

(*a*) Contributions on original scientific work,

(*b*) Reviews of recent advances in selected branches of analytical chemistry,

(*c*) An exhibition of new scientific apparatus.

After the Symposium there will be a half-day Conference on April 13, dealing with the teaching of analytical chemistry. All delegates are invited to attend.

The social programme will include a civic reception to the delegates and their ladies, a Symposium dinner, informal luncheons and dinners and a special programme for lady visitors.

Plenary lectures will be given by Prof. Dr. Ing. F. FEIGL (Brazil), Prof. R. BELCHER (U.K.) and Prof. P. W. WEST (U.S.A.). Already over 40 well-known analytical chemists from 12 different countries have agreed to contribute.

Application forms and further information can be obtained from: Honorary Symposium Secretary, M. L. RICHARDSON, A.R.I.C., A.C.T., c/o John and E. Sturge, Ltd., Lifford Chemical Works, Kings Norton, Birmingham 30 (U.K.).

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# FIFTEENTH ANNUAL LOUISIANA STATE UNIVERSITY SYMPOSIUM ON MODERN METHODS OF ANALYTICAL CHEMISTRY

(January 29–February 1, 1962)

An international symposium on modern methods of analytical chemistry will be held in Coates Chemical Laboratories, Louisiana State University, Baton Rouge, on January 29 through February 1, 1962. The program will consist of invited speakers only. Each of the ten speakers will have approximately two hours to discuss topics of current interest, and special time will be provided for questions and informal discussion.

The LSU symposia are provided as a means for giving exhaustive surveys of current topics. Outstanding authorities in the various fields concerned are brought in to discuss the history, theoretical aspects, instrumentation, technics, applications and future developments of his speciality. The programs are conducted on an informal basis so that a free exchange of ideas between delegates and speakers is obtained. The LSU symposia are unique in providing contact between distinguished foreign and American chemists.

In addition to the technical program, a display of modern laboratory equipment will be provided by leading apparatus manufacturing and supply houses.

*Fees.* The registration fee for the Symposium, including tickets for the mixer and banquet, will be $16.00.

*Place.* All lectures will be held in the main lecture room of the Coates Chemical Laboratories on the campus of Louisiana State University.

*Housing.* Housing is available on the campus in the newly renovated adult education center, Pleasant Hall. Pleasant Hall is designed to house guests to the campus who are attending various educational conferences, such as the analytical symposium. Pleasant Hall is completely air-conditioned, and the accommodations are comparable with those of any first-class hotel. Rates are from $2.50 to $5.00 per person per night. Persons desiring to stay in downtown hotels or motels should make their own reservations or make arrangements through their local travel agents. A number of excellent motels and hotels may be found conveniently located near the University.

*General Information.* All correspondence concerning registration and housing should be addressed to Short Courses and Conferences, General Extension Division, Louisiana State University, Baton Rouge, La. Questions concerning the program should be addressed to Dr. PHILIP W. WEST, Boyd Professor of Chemistry, Louisiana State University, Baton Rouge, La. (U.S.A.).

## PROGRAM

Professor RALPH ADAMS, University of Kansas (Lawrence)
*EPR in Investigation of Electrode Processes*

Dr. L. S. BIRKS, Naval Research Laboratory (Washington, D.C.)
*The Electron Probe*

Professor DONALD DAVIS, Louisiana State University (New Orleans)
*Chronopotentiometry*

Professor L. ERDEY, Technical University of Budapest (Hungary)
*Fusion Reactions* and *Morphological Structure of Precipitates*

Dr. R. NORMAN JONES, National Research Council (Ottawa, Canada)
*Raman Spectroscopy* and *Infra-red Spectroscopy*

Dr. KURT KRAUS, Oak Ridge National Laboratories (Tennessee)
*Ion Exchange*

Dr. J. E. LOVELOCK, National Institute of Medical Research (London, England)
*Detector Systems for GLC*

Mr. JOHN MITCHELL, Du Pont (Wilmington, Del.)
*Analysis of High Polymers*

Professor W. W. MEINKE, University of Mcihigan (Ann Arbor)
*Activation Analysis*

Dr. ALAN WALSH, C.S.I.R.O., (Australia)
*Atomic Absorption Spectroscopy*